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OF THE

ROYAL SOCIETY

OF NEW SOUTH WALES

FOR

1948

(INCORPORATED 1881)

VOLUME LXXXII

Parts I-IV

EDITED BY

W. B. SMITH-WHITE, M.A., B.Sc.

Honorary Editorial Secretary

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN

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Part II †

* Reprints of this article will be issued on completion of the Series.

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* Published February 21, 1949.

† Published September 5, 1949.

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* Published October 18, 1949.

† Published March 15, 1950.

NOTICE.

The Royal Society of New South Wales originated in 1821 as the " Philosophical Society of Australasia " ; after an interval of inactivity, it was resuscitated in 1850, under the name of the " Australian Philosophical Society ", by which title it was known until 1856, when the name was changed to the " Philosophical Society of New South Wales " ; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

TO AUTHORS.

Particulars regarding the preparation of manuscripts of papers for publication in the Society's Journal are to be found in the " Guide to Authors," which is obtainable on application to the Honorary Secretaries of the Society.

FORM OF BEQUEST.

I bequeath the sum of £ to the Royal Society of New South Wales, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[*Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.*]

The following publications of the Society, if in print, can be obtained at the Society's Rooms, Science House, Gloucester and Essex Streets, Sydney.

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ISSUED FEBRUARY 21, 1949

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EDITED BY
W. B. SMITH-WHITE, M.A., B.Sc.
Honorary Editorial Secretary

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VOLUME LXXXII

Part I

PRESIDENTIAL ADDRESS

By J. A. Dulhunty, D.Sc.

Delivered to the Royal Society of New South Wales, April 7, 1948.

Part I. GENERAL.

Ladies and Gentlemen,

It is with great pleasure, after a year's careful observation of the inter-relationships of the Royal Society of New South Wales with the international community of science on the one hand, and the people of our own community on the other, that I can report confidently on the steady progress of our Society. I think it is fair to say that that Society stands as high today as ever it did in the public esteem, and that the increasingly wide circulation of our journal—it has increased about 23 per cent. during the year—is evidence that the published accounts of researches contained therein are of considerable interest in the world of Science.

During the year 35 original papers were accepted for reading and publication, the subject matter lying in many different branches of science. This is almost a 60 per cent. increase over the number of papers published in each of the last two years, and it would seem that the "spate of papers" anticipated by Dr. Lions last year might well be commencing to eventuate. Already there are distinct signs that there will be an even greater number of papers for publication in the year now commencing. It might well be expected that the new *Australian Journal of Research* to be published under the ægis of the Council for Scientific and Industrial Research will reduce the number of communications to the Royal Society, but there is no evidence as yet of any such effect.

Early in the Society's year the newly appointed Governor-General of the Commonwealth of Australia, the Right Honourable W. J. McKell, P.C., was graciously pleased to accept the office of Patron of the Society, and the Society was honoured by his presence, together with that of his daughter, Miss Betty McKell, at the Society's Annual Dinner in the Refectory of the Sydney University Union on April 1st, 1948. The Society was also honoured by the presence of its old friend the Minister for Education, the Honourable R. J. Heffron, and Mrs. Heffron, and of the Vice-Chancellor of the University of Sydney, Dr. Stephen Roberts, and Mrs. Roberts and several distinguished representatives of sister societies. Altogether, 110 members and guests attended the function which was considered an outstanding success.

During the year, despite the loss of six members by resignation, the Society's ordinary membership gained by nineteen, twenty-five new members being elected during the year. It is a great pleasure for me to be able to record that gain, and to note that death claimed none of our members during this past year. Also, it is a pleasure to record that our list of Honorary Members has been increased by the election of two very distinguished scientists, Sir Harold Spencer Jones, F.R.S., and Professor F. Wood-Jones, F.R.S.

The ordinary monthly meetings of the Society have been well attended. In addition to the reading of papers several short addresses and lecturettes have been given: " Submarine Canyons, with special reference to recent discoveries off the South Australian Coast ", by Dr. G. D. Osborne; " Some New American Research Tools ", by Dr. F. Lions; " Palæontological Work in the U.S.A.", by Dr. Ida Brown; and " Impressions of Chemical Research Activity in Great Britain ", by Dr. T. Iredale. The September meeting was devoted to a short Symposium on Some Aspects of Atomic Science, addresses being given by Mr. H. W. Wood (" Stellar Energy "), Dr. R. C. L. Bosworth (" Separation of Isotopes by Gaseous Diffusion)", and Dr. F. Lions (" Radio-active Tracers in Chemistry "). The July meeting was largely given up to a screening of sound films, whilst at the November meeting the Society's customary practice of commemorating great scientists was followed, Mr. J. B. Thornton delivering an address on Torricelli and Helmholtz, whilst Dr. K. Brown discussed the work of Semmelweiss and Simpson.

The usual five Popular Science Lectures were delivered during the months of May, June, August, September and October, and were well attended and greatly appreciated, both by members of the Society and by the general public. The subjects were " The Hunter River Valley—A Future T.V.A.? " by Mr. W. H. Maze; " Snakes and Snake Venom ", by Mr. J. R. Kinghorn; " Measuring the Face of a Continent—The Use of Radar and Photography in Mapping ", by Dr. R. L. Aston; " The Colouring Matters of Plants ", by Mr. R. M. Gascoigne; and " The Story of Goitre ", by Dr. H. R. Poate.

The Clarke Memorial Lecture was delivered in July by Professor H. S. Summers, D.Sc., on the subject " The Teachers of Geology in Australian Universities ", and was of great personal interest to geologist members of the Society.

The Clarke Memorial Medal this year was awarded to Dr. A. B. Walkom, D.Sc., for his distinguished contributions to palæo-botany, and I am sure that every member of the Society rejoices at this award to so old a friend of science and so distinguished a member of this Society as Dr. Walkom.

The time for the award of the Walter Burfitt Prize came round again during this year and the Council had considerable difficulty in making its selection. An important principle was established during the discussions to the effect that the Walter Burfitt Prize should only be awarded once to the same investigator. The Prize was eventually awarded to Dr. J. C. Jaeger, a graduate of the Universities of Sydney and Cambridge, at present resident in Tasmania, for his distinguished contributions to the science of mathematics.

This year too, for the first time, the James Cook Medal has been awarded. Members will remember that some few years ago an old esteemed life member of our Society, Mr. H. F. Halloran, made funds available to the Society for the founding of two medals to be awarded annually. The senior one of these, the James Cook Medal, is to be awarded for outstanding contributions to Science and human welfare in the southern hemisphere, and the other, the Edgeworth David Medal, is to be awarded to a younger scientist for outstanding contributions to learning. The distinguished first recipient of the James Cook Medal is Field-Marshall the Right Honourable Jan Christian Smuts, Prime Minister of the Union of South Africa. I am sure I express the pleasure of all members at our ability thus to show our appreciation of Field-Marshall Smuts and of his work, and to say that our Society is honoured by his acceptance of the award. The first award of the Edgeworth David Medal will probably be made during the forthcoming year.

Quite early in our year the Council received communications from the Association of Atomic Scientists, and the Emergency Committee of Atomic

Scientists, headed by Professor Albert Einstein, urging the Royal Society of New South Wales to do whatever it could in the work of educating the non-scientific community against atomic warfare. After some deliberation the Council decided to hold a Conversazione in the Great Hall of the University and to open its campaign by having some short addresses delivered during the evening. The function was duly held early in October and was well attended by members and their guests. The Society's distinguished Patron, His Excellency the Governor of New South Wales, Lieutenant-General John Northcott, C.B., M.V.O., who has had first-hand experience of the results of atomic bombing in Japan, delivered the first address, and was followed by the Chancellor of the University, Sir Charles Bickerton Blackburn, the Minister for Education, the Honourable Mr. R. J. Heffron, and the Acting President of the Society, Dr. F. Lions. The atomic education campaign is to be advanced still further in the near future by the Society.

It is gratifying to record that the finances of the Society remain in a healthy state, even though the accounts show a slight loss on the year's working. This has long been anticipated by the Council as a result of the " backing up " of printing for the Journal. It has, however, to be recognized that the rapid rise in the costs of printing in the last year or so seriously threatens the stability of the Society's finances, and it is worthwhile pointing out to members again the importance of a greatly increased membership of the Society.

During the year the Society had the opportunity of entertaining at afternoon tea some distinguished visitors from abroad—Dr. E. H. Booth, of the International Wool Secretariat, in April, 1947 ; and Professor Raymond Firth, of the University of London, in March of this year. The Society is adopting a deliberate policy of endeavouring to entertain distinguished visiting scientists whenever they are in Sydney, and the opportunity affords, and thus enabling members to meet them informally.

At the November monthly meeting the Society had the opportunity of extending one of those courtesies to a sister academy which helped so much to build the international brotherhood of science. At the request of the President of the Royal Society of New Zealand the Sidey Summer-time Medal was presented by the Acting-President to Dr. D. F. Martyn of the Mount Stromlo Observatory for his work on radar and the receipt of radio waves from the sun.

The library continues to expand and many of the gaps on our shelves because of the war have now been filled. I should like to take this opportunity to express not only my own but also the Society's sincere thanks to our Honorary Librarian, Mr. H. W. Wood, for the excellent work he has done in the library this year.

During the early part of my term of office as President it became necessary for me to proceed abroad at short notice in order to extend my studies on coal utilization. The Council granted me leave of absence, and Dr. Lions agreed to act and was appointed Acting-President for the remainder of the year or until I should return. Much of the work that usually falls to a President has consequently fallen on his shoulders, and I should like here to express my thanks to him for so willingly carrying on. It is also in order for me here, also, to say just a few words in appreciation of the work of the other members of my executive, who are all retiring from their executive positions this year. First, Dr. Mellor has been the Editorial Secretary of the Society for a good many years now. It is to his wholehearted and enthusiastic work that the Society owes much of the esteem in which its Journal is held abroad. His modernization of its format has saved the Society very considerable expense, and his careful editing has helped in securing and maintaining the present high standard of our Journal. The Society will always owe to Dr. Mellor a very great debt of gratitude.

Then, although Dr. Osborne, our retiring Honorary Treasurer, and Mr. Morrison, our retiring Honorary Corresponding Secretary, have not had such a long period of service as Dr. Mellor, they have done excellent work for the Society, and I do want to tell them that that work is very greatly appreciated.

I come now to the second part of my address.

PART II. SOME NEW HORIZONS IN COAL UTILIZATION AND RESEARCH.

The structure of modern civilization has evolved in such a way that it now depends on fuel-energy, derived from coal and petroleum, for practically all its activities. Its needs have become so great that the value of coal and petroleum produced each year represents almost half the total value of all mineral production. This trend is progressing more rapidly as time goes on, and it appears highly probable that it will continue to do so during the next century of progress, resulting in a steadily increasing demand for energy now obtained from coal, petroleum and natural gas.

Scientists and technologists are faced at present with difficult problems regarding the future of the coal industry in relation to world requirements of fuel-energy, and questions of utilization, conservation of resources, and planning of research are receiving a great deal of attention in the principal coal-producing countries of the world.

COAL CONSUMPTION AND POWER REQUIREMENTS.

Looking back over the last one hundred years, progress and expansion of industry and transport resulted in a rapid increase in world production of coal up to about 1910, when it reached approximately 1,200 million tons per annum. Since then industry and transport have continued to expand and grow at a greater rate than during the latter half of the nineteenth century, but production of coal has increased but little, remaining at about 1,300 to 1,400 million tons. It follows that consumption has remained more or less constant for about 40 years, although demands for fuel-energy have increased very considerably. This appears to be a consequence of two major factors—more economic utilization of coal, and the contribution of petroleum to world requirements of fuel-energy.

Petroleum has met rapidly increasing demands for fuel in transport on the land and in the air, and also on the oceans where firing with fuel oil has largely replaced the use of coal. It has supplied some of the growing demands for stationary steam-raising plants and domestic heating, but its contribution in this respect represents only a small portion of increased requirements for heavy industry, gas production, generation of electrical power and railway transport, all of which depend almost entirely on coal. The fact that increased demands in these fields have not resulted in greater consumption of coal is evidence of successful application of results of scientific and engineering research to problems of fuel-economy. Overall efficiency of steam-raising plants and power units has risen considerably ; improvements in furnace efficiency have played an important part ; the use of gas and electricity for domestic and many industrial purposes, in place of solid fuel, has substantially reduced the amount of energy wasted or lost in using coal ; and important improvements have been made in industrial practice where coal or coke is used to supply heat for processing, as well as carbon, as in the case of the steel industry.

Looking into the future, it is generally believed that a great deal more economy is yet to be effected in the use of coal, and of gas and electrical power derived from it, and that consumption is not likely to increase appreciably while ample supplies of petroleum are available to meet rapidly increasing demands for liquid fuel. Unfortunately, reserves of petroleum are limited, and uncertainty regarding its useful life, and the extent to which coal may be called upon in the future to meet requirements now supplied by petroleum, gives rise to problems of a difficult nature.

It is not possible to assess the life of petroleum reserves in terms of a definite number of years, as they are unlikely to become exhausted at any particular stage. New fields are being developed as time goes on, and enormous reserves almost certainly remain to be discovered in the crust of the earth. Statistics show, however, that old fields are being used up more rapidly than new fields are being discovered. This means that an increase in production, at any time in the future, will result in a subsequent decrease below present day figures until available reserves are restored by development of new fields. Improved technique, and greater efforts by petroleum geologists and engineers in the development of new fields, will no doubt speed up the rate at which new fields are made available in the future, but this advantage will probably be more than offset by increases in annual consumption of liquid fuel. It appears, therefore, that a world shortage of petroleum is inevitable in the future, although oil wells will continue to flow for many years to come.

It is difficult to forecast when a permanent shortage will develop as a result of the excess rate at which old fields are being exhausted. It will probably commence to be felt very soon, in fact it is even possible, if not probable, that shortages of petroleum products at present existing in many countries may never completely disappear but will gradually become permanent. The present shortages are not due entirely to international economic difficulties, but rather to the fact that present-day consumption of liquid fuel is so great that production is unable to meet demands. During the present winter, a temporary peak in consumption has made it necessary for the United States to cancel all exports of petroleum products to enable her to carry on with minimum supplies, although production of oil in that country at present represents an all-time record.

To the scientists and economists responsible for planning utilization and development of national fuel resources, the existing situation presents many strange problems and uncertainties. If the present rate of consumption of coal continues to remain more or less constant, as it has for the last forty years, the coal resources in most countries represent considerable reserves. If, however, deficiencies in fuel-energy, due to permanent and increasing petroleum shortages, are to be met by additional consumption of coal, reserves immediately assume much smaller proportions, particularly with respect to special types of high-grade coals. Such questions lead to philosophical speculation and they are difficult to answer with any degree of certainty ; however the time has arrived when they must be given serious consideration.

Methods of producing liquid fuel from coal by hydrogenation, or complete gasification and hydrocarbon synthesis involving principles of the Fischer-Tropsch process, are well established and were practised on a large scale in Germany before and during the war. Large quantities of oil and petrol can be produced from coal, but the processes are complicated, requiring enormous outlays in specialized and expensive plant, and cost of production is relatively high. In fact, the production of large quantities of oil from coal could be regarded as an outstanding achievement in industrial chemistry, rather than a simple and economical way of meeting the world's liquid fuel requirements. Furthermore, it would consume large amounts of coal of which reserves are not unlimited. In view of these facts the necessity to depend on coal oil in place of petroleum, so simple and economically obtained, would in some ways seem to be a retrogressive step which may even hinder or modify trends of modern progress in industry and transport. It is difficult to imagine that such a change could take place. In the past, when facilities have become inadequate for the requirements of advancing civilization, ingenuity and inventive skill always seem to have provided new and more efficient facilities, helping to forward progress rather than retard it. If such philosophy is sound, and if the approaching petroleum shortage really constitutes the failure of a facility to meet the requirements of modern progress, then it would appear reasonable to predict that some new source of energy may be made available in the near future to do the work which has proved too great for liquid and solid fuels. Perhaps this is already heralded in recent discoveries of release of atomic energy and in the intensive research on its utilization now being undertaken. Relatively small resources of the particular forms of uranium, so far used, have been sighted as possible limiting factors in the widespread use of atomic energy. However, in view of results obtained from research in nuclear physics during the last twenty years, the release of energy from all radio-active elements would not be an unreasonable expectation in the near future. In fact, the ultimate achievement of releasing energy from non-radio-active elements, of unlimited abundance, would not be any more fantastic at this stage than present accomplishments appeared only twenty years ago.

The way in which atomic energy could be used to replace all solid and liquid fuels is as yet obscure, but it is not difficult to visualize the normal sequence of events which could lead to such an end. Unfortunately the majority of nuclear physicists are still engaged in researches other than those directed towards everyday use of atomic energy, but some work is being done on the development of experimental plants for generation of electrical power. The successful operation of such plants may eventually save enormous quantities of coal at present used in supplying electricity for industrial, domestic and transport purposes. Furthermore, the availability of electricity wherever required would encourage the existing tendency to change over from the direct use of coal to the use of electrical power and heating, and thus conserve additional quantities of solid fuel. In this way it appears as though the first applications in the general use of atomic energy may relieve consumption of coal more than petroleum. However, with the more general use of electricity, petroleum now used for diesel power and domestic heating would be conserved, and eventually smaller atomic energy plants for steam-raising may possibly be adapted to large passenger and cargo ships now traversing the oceans of the world and consuming as much as one ton of fuel oil per mile. Such advances would conserve petroleum products for use in air and road transport, and future research in the transmission of electrical power may even provide facilities for the use, in these fields of transport, of electricity generated at large atomic power stations.

In view of the possibility of atomic energy eventually effecting a large reduction in consumption of coal, questions arise concerning the future of the coal industry. It appears most unlikely that coal will lose its status in the mineral industry. It already holds an important place in the chemical industry, indirectly supplying, through by-products of the gas and coking industries, raw materials for an almost endless variety of products. Many of these, such as the plastics, are rapidly becoming essential commodities of everyday life, and will continue to be used more extensively in the future. Demands for raw materials in the " synthetic " industries are already so great that supplies of by-products from coal carbonization are rapidly becoming inadequate and research is being carried out, in England and America, on production of raw materials directly from coal in much larger yields than obtained by carbonization. The most promising results have been obtained by alkaline oxidation of coal, using air, or oxygen, under pressure and at slightly elevated temperatures. Mixed organic acids produced in this way, and suitable for use in the chemical industry, represent as much as 60% by weight of the coal oxidized, and their value over and above probable cost of production far exceeds that of coal as a fuel. Other investigations are being undertaken on specialized forms of solvent extraction, and chemical interaction between the " coal molecule " and various reagents, with the object of producing substances of more complex nature, and varied use in chemical manufacture, than organic acids from oxidation.

Recent advances have also been made in the manufacture of industrial carbons and low-priced structural materials for building and engineering construction. This work, which promises to open a new and important field of coal utilization, has been developed in the laboratories of Powell Duffryn Technical Services Ltd., England, and commercial production is already being undertaken. The processes involve pressure-moulding of very finely powdered coal followed by slow carbonization. This is so controlled that polymerization, associated with thermal decomposition, proceeds more rapidly than evolution of volatiles, which, together with development of plasticity during coking, results in a hard, fine-grained, carbonaceous product possessing the form into which the original powdered coal was moulded. The materials have many useful properties previously found in more expensive products made from graphite on one hand and thermo-hardening resins on the other, and they are almost certain to find a wide range of application in the future.

Such trends in coal utilization may well promote coal to a raw material of greater value than it now represents as a fuel, and belie fears for the coal industry should atomic energy eventually replace solid fuels to any appreciable extent.

Considerable progress has been made, over a number of years, in the use of pulverized coal for steam-raising in power stations and other large units, and it has extensively replaced stoker-fired furnaces in stationary plants in many countries. Rapid progress is now being made in research on the use of pulverized fuel in gas turbines and jet propulsion, in both stationary and mobile units. This technique eliminates steam-raising and steam-powered engines in the process of obtaining motive power from coal. It involves burning of powdered coal to produce high-velocity gases which pass over turbine blades providing power directly from energy released during combustion of the coal. Gas turbines offer certain advantages in stationary plants but their use is not likely to increase overall efficiency of energy transformation. In mobile units, such as railway locomotives, a very substantial increase in efficiency is indicated. In American projects, in which experimental gas turbine locomotives are already making test runs, an overall efficiency of about 15% to 17% is claimed, representing approximately twice the efficiency of steam powered railway engines. In the experimental locomotives coal is powdered on the engines by placing it under compressed air and then releasing pressure suddenly, which results in disintegration of the coal particles by a " bursting " effect. The locomotive is actually driven by electric motors powered from generators coupled to the turbines.

The use of gas turbines promises to increase the efficiency of coal utilization in railway transport by as much as 100%. This would constitute an important step in the contribution of research to more economical use of coal, mentioned earlier as a major factor in keeping annual consumption of coal more or less constant for the last forty years, although demands for fuel energy have increased continuously.

The foregoing speculations regarding deficiencies in adequate petroleum resources, and the use of atomic energy gradually replacing present-day fuels, may appear somewhat vague and unrealistic, but they must be taken into consideration in planning long-term programmes for fuel economy and research. Truly fundamental research, usually carried out in universities or institutions where work can proceed independently of immediate industrial requirements, need not be directly influenced by existing and likely future trends in coal utilization. It must continue so as to provide a fund of new knowledge about coal for use as required by changing economic and industrial conditions. Fundamental research of this nature is best guided by experience in recognizing problems arising out of recent results and planning investigations along lines most likely to supply data which can be assembled to produce significant results. Applied research, including fundamental work undertaken to provide a result needed for immediate application, must be planned with respect to current problems and probable future developments in industry. It is in this field that scientists and technical authorities are faced with rapid and far-reaching changes already commencing to appear in coal utilization. Problems arise regarding relative urgency of work on projects such as combustion of coal in grate-fired boilers, as powdered fuel, or in gas turbines ; widening the range of coal types used for particular purposes to meet dwindling, or unfavourably distributed reserves ; production of liquid fuel from coal on a scale proportional to a country's total requirements ; greater fuel economy in any particular industry ; or conservation of special coal types which may be required for future industrial developments.

During the recent nationalization of the coal industry in the United Kingdom, a careful scientific survey was carried out by the Department of Scientific and Industrial Research to obtain data showing reserves of coals required for various purposes such as production of gas, domestic coke, metallurgical coke ; and for domestic heating and steam raising in power stations and railway locomotives. The survey was based on data accumulated by the Geological Survey and Coal Survey over a number of years, and information from all colliery holdings obtained for purposes of assessment during the nationalization of the mines. In interpreting results it was assumed that research would continue to improve efficiency in utilization, as it had in the past, and that no great increases in consumption of coal were likely in the near future, although expansion in both domestic and industrial usage was almost certain. On this basis it was shown that reserves of all kinds of coal in the United Kingdom were ample for the next one hundred years at least. As a consequence of this finding, a general policy, although not officially stated, appears to have been adopted that there is no urgent need for drastic measures restricting the use of certain kinds of coal, or for intensive research programmes in fuel economy in addition to those already being undertaken. This would seem to bear special significance in view of the fact that one hundred years is a very short period of time in relation to the history of British industry, and to the nation's future progress. It suggests that authorities in a position to judge believe atomic energy will be used, probably in electrical power generation, so extensively in one hundred years time that coal, as a fuel, will not be of the same national importance as it is today. Electricity is at present replacing gas and solid fuel for all domestic purposes, and is taking the place of steam power in industry and railway transport, so rapidly that coal consumption will be reduced very considerably as soon as atomic energy is used in large power stations, as would seem to be its first and logical point of application.

No special programmes of research, or technical development, are being launched in the United Kingdom to meet the world shortage of petroleum, which appears imminent in the near future. England is accustomed to depending on external supplies of petroleum, and large reserves in the Middle East will probably be available longer than America's internal supplies. Furthermore, it is realized in England that processes such as hydrogenation and Fischer-Tropsch synthesis are available if, and when, required and that oils and petrol produced in this way are at present relatively expensive owing to high cost of coal production. In view of this it is felt that the most useful contribution to production of liquid fuels is first to reduce the cost of producing coal, by improved and more efficient mining technique, thus serving the dual purpose of providing industry with cheaper fuel as well as lowering the cost of liquid fuels from coal if their production should become necessary. This does not mean that research on production of liquid fuel has been neglected in England. A great deal of fundamental work on principles involved in Fischer-Tropsch and hydrogenation processes has been carried out at the Greenwich Fuel Research Station and other places, and work on Fischer-Tropsch synthesis is being continued. Large-scale production of petrol from coal by hydrogenation was carried out by Imperial Chemical Industries Ltd., at Billingham-on-Tees, before the recent world war, and large quantities of aviation fuel were produced in their plant during the war by hydrogenation of creosote oil from the gas and coking industries.

In America it is considered that demands for liquid fuel are increasing so rapidly, and shortages of petroleum are so advanced, that production of liquid fuels from coal will be necessary in the very near future to relieve consumption of petroleum products upon which the country's economy and progress largely depend. As a result of this situation, and reluctance to rely on imported oils, large funds are being made available from government as well as private sources for the establishment of commercial scale plants to produce liquid fuels from coal, and also investigate improvements and modifications in the processes. In addition, preparations are being made to synthesize petrol from natural gas by a modification of the Fischer-Tropsch process, and attention is being paid to production of oil from oil shales of which there are very large reserves, but coal is regarded as the main source of future internal supplies of liquid fuel. The country is fortunate in possessing large reserves of coal which would certainly provide all requirements of both solid and liquid fuels for several hundreds of years to come. Both hydrogenation and Fischer-Tropsch plants are being developed, and important improvements are claimed in the latter. It is anticipated that it will be possible to produce petrol at a little less than twice the cost of refinery petrol, using coal costing ten to fifteen shillings (sterling) per ton.

Coal Research.

During the last 50 to 60 years a great deal of progress has been made in geological, chemical and physical research on the occurrence and nature of coal; in mining engineering on production of coal; and in fuel technology and industrial chemistry on its utilization. Work in all these fields has been stimulated by the fundamental importance of coal in industry and national economy, and by increasing demands for larger quantities of coal and for more efficient and varied utilization, which have provided a wide range of problems requiring urgent investigation.

Field Geology.

Early in the development of a coalfield, field geology plays an important part in revealing occurrence of coal and its distribution beneath the surface. Areas of coal-bearing strata are located, and surveys are carried out to produce geological maps and sections showing outcrops of the coal measures and their underground extensions, depths beneath the surface, and varying thicknesses. As data from bores and shafts become available, more detail surveys are carried out to determine variations in thickness of individual seams, and the general nature of underground structures such as regional folds and faults. Having carried this work as far as available data will permit, field geology is able to assist and advise when faults and other irregularities are encountered in mining operations, but there is a tendency to feel that there is not a great deal more it can do to help coal production in the established coalfield. Recent work, however, has shown that field geology can serve an important purpose even in well-developed coalfields. By a detail study of underground structure it is possible to produce structure-contour maps for any one seam or several seams, showing minor folds, domes, or basins superimposed on the general dips or regional structures of the coal measures as a whole. A limited amount of this work has been carried out in some of the English and American coalfields, and it was commenced in Germany before the war, while in Australia it has been pioneered by E. A. Rudd (Geologist, Broken Hill Prop. Co. Ltd.) in the New South Wales coalfields. Rudd's work—prominent in this field—and its advantageous application in modern coal mining, were dealt with in an address delivered to colliery proprietors in the southern coalfield (Rudd, 1946). The detail structure-contour maps are of considerable value in planning colliery development well ahead of the actual working face, as is essential in modern mechanized mining. In the case of the New South Wales coalfields, Rudd's work has shown that features such as thickness of seam and ash content may vary with structure. In some seams thickness and ash content both increase towards the synclines and decrease on the anticlines, indicating contemporary folding with deposition of coal-forming débris. This result, which does not appear to have been established in overseas coalfields, provides valuable information from which seam conditions and coal qualities may be predicted, in addition to dips and grades, and used in planning development.

Another field of geological research likely to become important in the coal industry is the study of causes of rank-variation from the viewpoint of metamorphic environment. Little has yet been accomplished, but preliminary results have attracted attention in some of the British and German coalfields. In areas where analyses of coal are available from a number of points, " iso-vols " or " iso-carbs " (representing lines of equal rank) are plotted on a map. In almost all coalfields areas treated in this way exhibit some orderly trends in rank-variation, either about a centre or across the area. Having obtained the rank-variation map, the geologist is able to investigate causes of rank change. It may be due to unequal loading with superimposed strata associated with differential sinking during deposition, or subsequently. It may also be due to heat from intrusive igneous bodies, or to unequal distribution of pressure and heat developed by lateral forces and local folding of the measures, or even to topographical relief existing on a surface uplifted and eroded soon after deposition but removed later by peneplanation. If the cause of rank change can be determined for a particular coalfield, it is then possible to predict rank-variation beyond the limits of the area in which it is known, by studying the regional behaviour of the responsible factor. It is believed that results of this nature will throw new light on processes of coalification, and provide important data for estimation of reserves of different kinds of coal and for planning future coalfield development. The results of ultimate and proximate analyses, for representative seam samples, have been used as a basis for rank-variation. This is not entirely satisfactory, as lateral changes in proportions of banded constituents in the coal may introduce errors greater than variations due to rank differences. It is felt that greater accuracy is required, and that analyses of pure vitrain separated from the coal should be used, or possibly a more precise means of measuring rank such as some physical or optical property of the vitrain.

Observations have been made, and investigations carried out, for many years in connection with the behaviour of coal measure strata during subsidence from mining operations in both America and England. Specialized research on strata control is now being carried out by the Safety in Mines Research Board at Sheffield, in England (Phillips, 1946). This has introduced another new field of geological work in which the study of advanced tectonics is being applied to problems regarding distribution of forces, and stability of strata, associated with coal mining operations. The properties of different rock types are being studied with respect to critical forces in breaking, shearing and bending, and investigations are being made of distribution of pressure forces in roof, walls and floor sediments of mine workings, and also concentrations of pressure in underlying and overlying beds, with the object of determining maximum size and nature of safe excavations for the particular rocks with which any seam is associated. It has been established that mine workings may be disturbed, and dangerous falls of rock caused, by local concentrations of pressure due to mining operations in seams at higher levels. Results of this work are likely to prove very important in planning new mining operations with greater safety, and general economy of production, particularly where several seams are to be worked at different levels in the same locality.

Stratigraphical Correlation.

Closely associated with field geology is the application of micro-palæobotany to problems of stratigraphical correlation of coal seams, where continuous outcrops cannot be mapped and where horizons with typical macro-fossils, or distinctive lithological features, are absent. The study of microspores has been used successfully in some cases, and promising results are being obtained, although the method is not yet fully established. Limited vertical ranges or the presence and absence of specific microspore types in different sections of a coal measure series has so far proved the most reliable in correlation.

The use of characteristic assemblages was originally believed to be the most logical and satisfactory method, as the assemblage was considered to represent the plant community which contributed to the coal-forming débris of a particular seam. Recent work, however, has shown that different coal types, particularly bright and dull varieties, contain different assemblages at the same place in a seam. This is an important factor as the normal method of sampling, involving a vertical channel sample across the seam may introduce errors owing to variations in relative proportions of " brights " and " dulls " from place to place. Very little work has yet been done on the persistance of assemblages in the bright and dull sections of coal seams, and there does not appear to be any general agreement as to whether the two coal types should be sampled separately or not in studying seam assemblages. The reason for different assemblages in bright and dull coals is somewhat obscure, but it may be related to differences in conditions of accumulation producing the two coal types. The dull coals, containing a high proportion of subaqueous, swamp vegetation, are believed to represent peat formed beneath a covering of shallow water, whilst the bright coals derived largely from coarse woody material, probably originated from a peat bed the surface of which stood slightly above water-level. These conditions would certainly favour different types of vegetation, resulting in the preservation of different microspore assemblages in each case.

Classification.

Many different systems have been devised for the classification of coals, based on chemical and physical properties, palæobotanical features, geology of occurrence and economic uses. Some have found application in restricted fields of research or utilization but none has proved satisfactory for universal adoption by all concerned with coal, in all countries of the world. An excellent review of coal classification has recently been made by R. A. Mott (1948) of the Midlands Coke Research Association, in England.

Coals vary in several different ways over a very wide range, and no one coalfield contains coals representing all variations. People with different interests look upon coal variation from entirely different viewpoints, and in the majority of cases classifications have been based on a limited range of variation found within one coalfield, or a group of coalfields, in one country. They have usually been devised to meet the requirements of a restricted field of interest rather than all purposes for which coal classification is required. Some of the individual systems have approached the necessary requirements for universal adoption, but they have not really provided a common language in which the geologist, chemist, coal miner and coal user can reach an understanding. As a result of this situation a general and rather vague classification appears to have evolved somewhat of its own accord, embodying certain desirable features of many different schemes. It is best described as classification by rank, type and grade, and its underlying principles are becoming understood and used in all fields of interest in all countries. This classification takes into consideration the three independent variable factors responsible for all kinds of coal and their different uses. The rank of a particular coal is the stage it has reached in the natural process of coalification. It is commonly described in terms such as brown coal, bituminous coal or anthracite, while intermediate or special stages are referred to in terms such as low-rank bituminous, coking bituminous or semi-anthracite. Foreign countries employ terms with equivalent meanings, such as the German usage of braunkohle, steinkohle and anthrazite for major rank subdivisions, and flammkohle, fettkohle and magerkohle for the intermediate or special stages referred to above. Type variation is related to the nature of the original organic débris from which the coal was formed. Types commonly recognized include the bright and dull varieties of normal humic coals, the cannel coals, and the torbanites or boghead coals. Of these the normal humic coals are derived mainly from coarse remains of wood, bark and leaves accumulated and preserved under conditions which produce bright coals containing an excess of vitrain and clarain, or produce dull coals consisting mainly of durain. The cannel coals are derived from finely divided plant remains with spores and resin, while the torbanite or boghead types are produced essentially from algal débris. Each coal type exhibits rank variation throughout its particular metamorphic series. The third variable factor is grade, influencing the usefulness or quality of any coal type of any rank. It depends on the amount of mineral matter introduced during deposition, and the coal is usually described simply as high, medium or low grade, with respect to its ash content.

The terminology of this general system of classification has not been specifically defined, but all coals can be described by using three terms, referring to rank, type and grade, all of which may vary independently. A statement such as "bright, high-grade, coking-bituminous coal" is clearly understood by all concerned with coal, and at the same time has a definite scientific meaning. For more exact designation the user of coal may specify grade in terms of ash percentage, or use B.T.U. values and size grading; the chemist or geologist may refer to rank in terms of percentage of volatile matter or carbon; the palæobotanist may describe a particular type by using generic names of predominating plants, but the same general underlying system of classification prevails. There is much room for refinement of the system and standardization of terminology, but its clarity and simplicity must be maintained, otherwise it will not be universally understood and used, and will immediately lose its value as a classification.

The most useful research in coal classification would seem to be further clarification and improvement of the general system already adopted in principle, rather than attempting to formulate new and novel schemes with strange terminology and limited application. Furthermore, it appears most important that research should be designed to make a contribution to coal classification, rather than the classification of coal in a certain country or coalfield.

Petrology, Coalification and Fundamental Nature of Coal.

Research of this kind is of a purely fundamental nature, but results usually find direct or indirect application in some practical field almost as soon as they have been established. Facilities, however, for true fundamental research on coal are relatively limited in all parts of the world, apparently because the research worker cannot always be certain of the nature of data he is likely to produce, and also because the true value of his results, in the field of practical problems, is difficult to appreciate until after they have found application.

Work in coal petrology has made good progress in recent years. Early work led to an understanding of relations between the macro- and micro-constitution of coal, and more recent work has placed coal petrology on a firm and quantitative basis. Once a clear conception of the micro-constitution of coal (recently reviewed ; Dulhunty, 1946) was established, detail studies were possible of the specific nature of the macerals and banded constituents, and their relations to properties of different coal types. This is leading to a clearer understanding of how coal types vary and why each behaves as it does in commercial utilization.

Research in America, initiated by Thiessen (1947) and his colleagues at the United States Bureau of Mines, has made important contributions to coal petrology. Highly efficient methods have been developed for cutting thin sections across the full thicknesses of coal seams, studying the micro-constitution of coal types, and making petrographic analyses of coal seams. It has been shown that many properties, important in utilization, can be correlated with-micro-constitution and predicted from results of petrographic analyses, particularly in cases where type and structure of coal are more significant than its rank. For example, it has been established that vitrinite is far more reactive to hydrogenation than fusinite ; that it is responsible for agglutinating properties during coking ; and that the two constituents give different proportions of mixed organic acids on mild oxidation. Petrological work of this nature is already finding application in the evaluation of coal for industrial purposes such as coking, hydrogenation and low-temperature carbonization, and it appears highly probable that it will provide important data in connection with the use of coal for production of liquid fuels and chemicals.

In England, the work pioneered by Stopes, Wheeler and Seyler has thrown a great deal of light on the palæobotanical structure of coal, and established a basis for the microscopical study of macerals making up the banded constituents. Seyler's more recent work on the reflectivity of coal macerals, or the amount of vertical incident light reflected from polished surfaces, has produced interesting and surprising results (Seyler, 1941). He maintains that reflectance, which increases from vitrinite to fusinite, does not vary continuously but rather by nine steps or values, and that there is a constant ratio between the reflectance values of any two successive steps. All macerals derived from plant tissue appear to conform to one of the nine values termed components in the vitrinite-fusinite series. In the early stages of coalification plant tissue would seem to undergo differentiation into macerals representing a wide range of components. As coalification proceeds beyond lignite rank, reflectance values are stepped up by metamorphism and the macerals pass from lower to higher components. This suggests some kind of fundamental mechanism governing progressive changes from slightly altered plant material to the highly complex substances in bituminous coals, and may indicate the existence of a series of specific chemical structures, or physical conditions, representing steps in the polymerization processes associated with coalification. When satisfactorily established and interpreted, Seyler's results promise to provide new and extremely valuable techniques for quantitative determination of rank in coal, and for the study of chemical and physical properties dependent upon rank variation. Nothing, however, has yet been established regarding the significance of his discovery, and the apparent absence of any step-wise variation in all known chemical and physical properties of coals has caused a certain degree of reluctance in accepting his findings. Further investigations, and verification, of discontinuous variation in reflectance and other properties is urgently needed, and will probably constitute an important field of petrological research in the future.

The more botanical aspects of coalification are being studied actively by Schopf (1947), Cady (1942) and others in the United States. Their work is gradually leading to a clearer picture of the preservation of various kinds of plant material, and the way in which they are changed into coal substances of lignic and cellulosic origin. It is also providing information regarding relative rates of change in coalification of specific plant substances such as spores, cuticle, normal woody tissue and products of humic degradation, and it emphasizes the existence of the two distinct processes of *vitrinization* and *fusinization.* It is generally agreed that both processes commence early in the history of coalification, and that woody material may follow either process of change without respect to its original type or nature, but the cause of differentiation still remains obscure. Most workers now maintain that fusain is a product of a process initiated soon after burial, but some still believe that it may possibly represent charcoal from ancient forest fires. The remarkable resemblance of fusain to normal charcoal, and its presence in some brown coals, appears to be responsible for theories claiming all fusain to be charred wood.

Recent observations made in peat and brown coal deposits in Australia, England and Germany strongly suggest that practically all fusain is formed by coalification after deposition and preliminary compression. In deposits of advanced brown coal rank, it normally takes the shape of pieces of wood compressed parallel to the bedding plane, and some fragments consisting partly of fusain and partly of vitrain exhibit the same amount of compression throughout. This would seem to indicate fusinization after burial, as hard brittle charcoal would be crushed or else retain its original irregular shape if strong enough to withstand pressure. In some immature deposits, however, where cover is small and the brown coal is so soft that pressure from overburden is of a hydrostatic nature rather than a vertical compressional force, occasional pieces of fusinized wood showing very little flattening are present, but such immature deposits seldom contain the proportion of fusain found in higher rank coals. In view of this, and the possibility of introduction of charcoal into peat deposits, it is felt that a small amount of the fusain in coal may represent wood charred before burial, but most of it almost certainly originated as a product of fusinization after deposition. It is highly probable that future research on chemical, physical and optical properties of constituents in low rank coals will provide a means of distinguishing between fossil charcoal and fusain formed after burial. Such results would elucidate the long-disputed origin of fusain, and make a valuable contribution to the study of coal constituents.

The most important progress in research on the fundamental nature of coal substance, during recent years, has been made in the field of physical chemistry and the work is becoming known as " coal physics ". The investigations (recently reviewed in detail—Dulhunty, 1946) were carried out mainly in England, and included the study of X-ray diffraction, rheological properties, sorption properties and surface chemistry, magnetic and electrical properties, and optical properties. Results have provided valuable information regarding the aggregational state of coal substance between microscopical and molecular dimensions, establishing coal as a highly polymerized substance in the form of an isogel with definite micellar structure. Some indication has also been obtained of molecular structures and packing within the micelles, and the study of coals varying widely in rank has given a reasonably clear picture of the evolution of the micellar structure during coalification. Also, it has been shown that many properties of economic importance depend largely on the physical condition of coal, as well as its chemical constitution. Research of this nature is essentially fundamental and progress is slow, although its importance is gradually becoming recognized and it is likely to take a prominent place in future investigations.

Chemical research on the nature of coal, and its metamorphic evolution, has made relatively little progress owing to difficulties encountered in studying its molecular structure without first subjecting it to processes of oxidation or thermal decomposition which produce substances bearing very little relation to the original coal molecule. The most useful information has been obtained by mild oxidation, partial hydrogenation and solvent extraction of different petrological constituents in coals of various ranks. Little conclusive evidence has been produced, but results generally indicate an increasing degree of aromatization in higher rank coals and in more fusinized constituents, associated with elimination of oxygen and hydrogen from the more aliphatic structures believed to be present in the humic degradation products of plant material. Progress in coal physics, however, has opened up a new field of attack for the chemist, and it is almost certain that the application of advanced techniques in physics and organic chemistry will, before long, provide a wealth of new knowledge about coal, so urgently needed for its more economical use as a fuel and as a raw material in the chemical industry, and for the solution of other problems in fundamental research.

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A GENS OF DALMANITID TRILOBITES.

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With Plates I-II.

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INTRODUCTION.

In the Palæozoic rocks of eastern Australia there is a closely related group or gens of genera and species of trilobites which has heretofore been covered by the single name *Dalmanites meridianus* Etheridge and Mitchell, 1896. The present study shows that this omnibus name has covered forms belonging to the genera *Dalmanites* and *Odontochile.* The group of species concerned includes :

Dalmanites wandongensis, sp. nov.
Odontochile meridianus (Etheridge and Mitchell).
O. loomesi (Mitchell).
O. formosa, sp. nov.

As " *Dalmanites meridianus* " has been relied upon as an index fossil, stratigraphical inaccuracies have resulted from including so wide a range of forms in one species.

In the genera *Dalmanites* and *Odontochile* there are often groups of closely related species which are difficult to differentiate. When describing the dalmanitid genera of North America, Delo (1935, p. 55) noted this feature. The biological inference is that there was a high mutation pressure in these instances, resulting in a group of closely related forms. The genera named are often prolific in numbers of individuals, and this would help in the preservation of a series of forms.

GENERA OF THE GENS.

Dalmanites Barrande, 1852, genotype *Trilobus caudatus* Brünnich, 1781 (see Delo, 1935*b*), groups together typical dalmanitids having an elongate, non-denticulate hypostoma, genal spines, and 11 to 16 pygorachial segments. The genus is restricted to the Silurian in Europe, but continues up into the Lower Devonian in North America. In Australia the range of *Dalmanites* is probably limited to the Silurian, but this cannot be determined with certainty as yet, as there are many unsolved stratigraphical problems relating to the boundary between the Silurian and the Devonian.

The diagnosis of this genus is unusual in that it relies on the hypostoma, which is preserved comparatively rarely, and very seldom *in situ.* It needs to be *in situ* if it is to be actually proved that it belongs to a particular species. The hypostoma is also a " conservative " part of the exoskeleton, varying little from species to species, and sometimes even from genus to genus. The diagnosis of *Dalmanites* is unusual, too, in that it cites no features of the dorsal side of the cephalon, whose morphology provides the chief *fundamenta divisionis* of families, genera and species in the Trilobita. Furthermore, the diagnosis depends on features of the pygidium, which also is generally a conservative part of the exoskeleton, i.e. its variations are usually so small and few that they do not assume taxonomic significance of generic rank. The biological inference from these facts is that while the trilobites of the Dalmanitidæ maintained the general dalmanitid impress, mutations took place in conservative parts of the exoskeleton, viz. the hypostoma and the pygidium. The diagnosis thus selects features which are taxonomically significant but not necessarily biologically important.

Odontochile Hawle and Corda, 1847, genotype *Asaphus hausmanni* Brongniart, varies from *Dalmanites* in having a denticulate hypostoma, and 16 to 22 pygorachial segments. Delo (1940, p. 55) found also that the larger size of *Odontochile* is a helpful guide. *Dalmanites* and *Odontochile* merge into one another, as is illustrated in the gens of *Dalmanites meridianus*. *Odontochile* arose out of *Dalmanites* and is limited to the Lower Devonian. The obvious close relationship of the Australian gens of dalmanitid trilobites now described makes it almost certain that in this case *Odontochile* arose in the Australian area from an Australian *Dalmanites*, and so independent of its genesis in other areas. *Odontochile* may thus consist of groups which have arisen in various parts of the world, and which are closely homologous and isochronous, but actually independent mutations or series of mutations. Evidence is accumulating in support of such a view for a number of fossils. Or to express it another way, because *Odontochile* is found in Australia and North America, it does not necessarily mean that the form originated in one area and migrated to the other. There are records of new mutations in living forms where the same mutation has arisen in different parts of the world at the same time. It would appear that genes have a tendency to alter their constitution in one direction rather than in others, and thus the same mutation may take place in what are apparently the same genes though in different parts of the world. If this is so, then mutations depend on some inherent structural factor as well as perhaps on some external influence (for instance, the influence of X rays on the mutation rate).

R. and E. Richter (1931) have pointed out how *Dalmanitina*, *Dalmanites* and *Odontochile* form a phylogenetic sequence.

The diagnostic features are unusual in *Odontochile* as they are in *Dalmanites*. In a mobile animal the anterior end is naturally more specialized, as it is nearest the sources of stimuli which guide its movements. The great amount of specialization in the anterior end (cephalization) readily provides a basis for classification, and that is why from the Arthropoda to the Mammalia cephalic structures possess both biological significance and taxonomic usefulness. The diagnoses of *Dalmanites* and *Odontochile* provide an exception to this general rule. Probably the addition of extra segments in the pygidium of *Odontochile* was not a development of much biological moment. It appears to be part of the general enlargement of the animal, and the advantages (as far as we can see) simply those of larger size and weight. The denticulate hypostoma of *Odontochile* probably gave more area for muscle attachment, and new angles of muscle action. However, the supersedence of *Dalmanites* by *Odontochile* must surely mean that the new structures were of some biological advantage. But we are limited by not being able to discover what changes there were in the soft parts of the animals concerned.

SOME SPECIES OF THE GENS.

Dalmanites wandongensis sp. nov.

Plate 1, figs. 1–4.

Phacops (*Odontochile*) *caudatus* McCoy, 1876, pp. 13–15, Pl. XXII, figs. 1-7; Pl. XXIII, figs. 7, 8, 9–10.

Type Material.

Holotype, consisting of the internal cast (steinkern) of a pygidium in bluish-grey, very fine-grained sandstone from "Wandong, near Kilmore", i.e. the Geological Survey of Victoria fossil locality Bb 18 on Broadhurst's Creek. The specimen was presented to the University of Melbourne Dept. of Geology by Mr. F. H. McK. Grant on 24.6.31, and is now Reg. No. 1946 in that department.

Two paratypes, consisting of counterparts of an almost complete cephalon inferred to belong to the same species, preserved in mottled greyish very fine-grained sandstone from "Wandong, Victoria", probably the same locality as the holotype. The specimens are Reg. Nos. 420A and 420B of the Department of Geology Museum, University of Melbourne. The counterparts are an internal cast or steinkern, and an external mould.

Description of Holotype.

About 27 mm. wide at anterior end, and 25 mm. long without terminal point, i.e. as actually preserved. The rachis is 6 mm. wide anteriorly, and 2 mm. wide posteriorly just before it is rounded off. There are ten pleural segments, the elevated portion of each being divided throughout its length by a median furrow. The anterior ribs are slightly deflected backwards, and this deflection is strongly increased about two-thirds of the distance to the margin. The amount of general deflection increases with each rib until the most posterior one is almost parallel with the median longitudinal axis of the pygidium.

Fourteen pygorachial segments can be counted. They are flattened and rounded at their ends in the anterior part of the pygidium where the segments are fully developed. The margin is entire. The perimeter of the pygidium describes a more or less equilateral triangle. The terminal spine is incomplete, but its morphology can be seen in McCoy's Plate XXIII, figs. 9–10. On the right side of the pygidium the doublure is shown; it is 2 mm. wide.

Description of Paratypes.

Cephalon sub-triangular in outline, the margin tending to form a point in front of the glabella. Cephalon tumid, rising about half a centimetre above the plane of the margin. Width 4 cm. and length 2 cm. The glabella is tumid but the eyes rise even higher than it. The axial furrows, if produced as far as the longitudinal median axis of the trilobite, make an angle of about 22°. The first (most anterior) pair of glabellar furrows are oblique, and make an angle of about 70° with the median longitudinal axis. The second and third pairs of furrows are transverse, narrow, and deep; neither reach the axial furrows. The neck furrow reaches the axial furrow, but the third and second glabellar furrows respectively have their outer ends progressively further away from the axial furrows.

The posterior margin of the cephalon makes an angle of about 60° with its lateral margin. The general spines are wide, and probably long (judging by the convergence observed on the part preserved, and McCoy's Plate XXIII, fig. 7).

The eyes are large and very elevated (Pl. 1, figs. 3–4). Anteriorly, they reach the end of the first glabellar furrow, and posteriorly they almost reach the neck furrow. The visual area is almost vertical, being directed slightly upwards and outwards. The visual area measures half a centimetre high by $1\frac{3}{4}$ cm. wide.

There are about 486 lenses in the eye, made up of 27 rows in the middle with 12 lenses each, and on each side of that, 10 rows with numbers gradually descending from 11 to 4 lenses per row. Thus there are 47 rows of lenses present. This description is made from the right eye, which is the better preserved, and which is present also in the counterpart. The external mould of the eye shows that the lenses were most strongly convex on their outer surfaces, while the internal cast shows that on their inner surfaces the lenses were also convex, though not so strongly. Each lens must therefore have been quite bulbous, and possessed of at least some of the properties of a " bull's eye " lens.

The external mould shows that the surface of the cephalon possessed a fine granular type of " ornament ".

Comment.

McCoy (Pl. XXII, fig. 3) figured a hypostome which is non-denticulate, thus providing further evidence that the genus is *Dalmanites.* The specimens figured by McCoy were housed in the National Museum, Melbourne, but some of them cannot now be located, including the cephalon (Pl. XXII, fig. 1). The number of segments cannot be counted on the pygidia available, except the specimen figured in Pl. XXII, fig. 6, but this is exceptionally wide and may well be a variant of the species as *O. loomesi* is of *O. meridianus.* All McCoy's specimens come from the same locality as the holotype.

Odontochile meridianus (Etheridge and Mitchell.)

Hausmannia meridianus Etheridge and Mitchell, 1896, pp. 504–509, Plate XXXVIII, figs. 1–8 ; Plate XL, fig. 1.

Dalmanites meridianus Mitchell, 1919, pp. 443–446, Plate XV, figs. 3–4 ; Plate XVI, figs. 6–7.

Type Specimens.

Etheridge and Mitchell did not name a holotype when they described their species in 1896, but in 1919, when Mitchell was describing the closely allied *O. loomesi*, he included in his plate XV a photograph (a drawing was published with the original description) of a complete specimen which he referred to as " the original type specimen of *Hausmannia meridianus* ". It is the obvious choice, and so this specimen may be regarded as the holotype and the other specimens figured in the original paper as paratypes. Mitchell figured three more pygidia belonging to *O. meridianus* in his 1919 paper (Pl. XV, fig. 4, and Pl. XVI, figs. 6, 7) and these may be regarded as hypotypes.

Generic Position.

Originally described as *Hausmannia*, the above species was later referred to *Dalmanites* by Mitchell (1919), but is now referred to *Odontochile* because the holotype has 17 pygorachial segments, and the form therefore falls within this genus by definition (more than 16 pygorachial segments). A hypotype figured by Mitchell (1919, Pl. XVI, fig. 6) shows 18 pygorachial segments.

Etheridge and Mitchell (1896, Pl. XXXVIII, fig. 8) figured a damaged hypostome, to which reference was not made in the text. In size and proportions it corresponds fairly closely to hypostomes of species of *Odontochile* in Victoria, but no denticles (such as are characteristic of that genus) can be seen in Etheridge and Mitchell's drawing.

Odontochile loomesi (Mitchell).

Pl. 1, figs. 5–6.

Dalmanites (*Hausmannia*) *loomesi* Mitchell, 1919, pp. 441–449, Plate XV, figs. 1–2; Plate XVI, figs. 3–5.

Type Specimens.

Mitchell did not name any types and so all his figured specimens must be regarded as syntypes. The first specimen figured (Pl. XV, fig. 1) is a complete carapace, and the description is largely based on it. This therefore is selected as a holotype and becomes the lectoholotype. The other specimens figured are lectoparatypes. Through the courtesy of Mr. H. O. Fletcher, palæontologist, Australian Museum, Sydney, I have been able to examine the lectoholotype, and rephotograph it (Pl. I, figs. 5–6).

Generic Position.

This species is referred to *Odontochile* because the lectoholotype possesses 16 pygorachial segments, and the lectoparatypes possess about 20 and 16 respectively. Describing the pygidium, Mitchell says: " Axis consists of 16 to 20 rings (dependent on the state of maturity)." The form therefore belongs to *Odontochile* by definition. In discussing pygidial segmentation, Mitchell (p. 445) mentions that Silurian forms do not have more than 16 segments, then states that his species has up to 20, but claims nevertheless that his species " shows transition towards the pygidial segmentation of the Devonian species ". He seems to have thought that Reed's (1905) definition of 12 to 16 segments for Silurian species referred to the number of pygopleural segments, whereas it refers to the number of pygorachial segments.

Odontochile formosa sp. nov.

Plate II, figs. 1–2.

Type Material.

A cast of a complete carapace constitutes the holotype (Univ. of Melbourne, Dept. of Geol., Reg. No. 882, presented by Mr. W. McCormack). It is preserved in bluish grey, very fine grained sandstone, which is very compact, so much so that the original calcareous material is preserved in some of the fossils, which is unusual in the Silurian and Devonian rocks of Victoria.

Locality.

The holotype was collected from a Country Roads Board quarry, 1¾ miles 20° W. of S. from Kinglake West (Tommy's Hut) Post Office. It is near the headquarters of Scrubby Creek, and the military map reference is Kinglake sheet 247,847.

Etymology.

The trivial name is derived from the Latin *formosus*, " beautiful in form ", a reference to the elegant proportions and well-developed structures of the species.

Whole Carapace.

The carapace is large, being about 16 cm. long and 9 cm. wide. The general outline is ovoid. Cephalon with large eyes and very long genal spines. Pygidium large and mucronate. Whole carapace covered with fine granulation. The carapace has been compressed dorso-ventrally, the greatest displacement taking place in the cephalon.

Cephalon.

Sub-triangular in outline. A flat border 3 to 4 mm. wide is shown on the left side of the cephalon, but as the frontal margin is not preserved, it cannot be proved whether this border extended right round the cephalon or not. As preserved, the cephalon is 3·2 cm. long and 9 cm. wide, a ratio of length to width of about 1 : 2·8.

The glabella is approximately 3·8 cm. wide anteriorly and 2 cm. wide posteriorly. There is a central longitudinal furrow in the frontal lobe, believed to be due to compression of a tumid carapace. The axial furrows, if produced as far as the median longitudinal axis of the trilobite, make an angle of about 50°. The first (most anterior) glabellar furrows make an angle of about 140°. The second and third furrows are more or less transverse, and reach the axial furrows. The free cheeks are moderately tumid for this genus. The marginal furrow and neck furrow make an angle of about 50° (left side of cephalon measured).

The eyes are large, reaching from the first furrow to the third. A line joining the ends of the left eye measures 1·5 cm. The facets are small, circular and closely packed, there being 12 or more (the preservation is not good) in the central rows, and less towards the ends. There are of the order of 40 rows.

The genal spines are long and strong. On the right side of the holotype an almost complete genal spine is preserved, but it is turned under somewhat by compression. As preserved, it measures about a centimetre wide where it leaves the cephalon proper, and reaches as far as the eighth segment of the thorax, where it is broken off, the width there being 2 mm.

Thorax.

The thorax consists of eleven segments, and is approximately 6 cm. long and 9 cm. wide, a ratio of 1 : 1·5. The greatest width of the axis is 2·5 cm., a ratio of axis to thorax of 1 : 3·6, and of axis to pleuron of 1 : 1·3. Each pleuron is divided by a narrow median furrow for practically its whole length. The outer ends of the pleura are deflected ventrally, and terminate in pleural spines.

Pygidium.

The pygidium has 18 pygorachial segments plus the rounded terminus. There are 12 pygopleural segments. The right half of the pygidium is partially obscured by the matrix, but judging by the left half the pygidium must be 9 cm. wide. The length (without the terminal spine) is about 6·5 cm., a ratio of width to length of 1 : 1·4. The mucro is broken, but was 1 cm. wide where it joined the rest of the pygidium. It appears to be narrowing rapidly.

The greatest width of the rachis is 1·7 cm. (i.e. about one-fifth of the width of the pygidium), and the smallest 0·5 cm. The rachis tapers gradually and ends before reaching the terminal spine. The posterior margins of the pygorachial segments nearer the thorax arch in the middle in an anterior direction. Like the thoracic axial segments, the anterior pygorachial segments have short furrows towards their ends. The posterior pygorachial segments become mere rings without specialized structure.

The anterior pygopleural segments are gently curved posteriorly. This curvature increases until the last segment is actually parallel to the longitudinal axis of the trilobite. A narrow median furrow is present in all the pygopleural segments. Each furrow commences at the rachis and terminates abruptly just before reaching the margin of the pygidium, which is fused into a continuous line. Where the pygidium is broken away a little, a well-developed doublure (of the order of ½ cm.) can be seen.

Comparison.

The new species simulates closely *Odontochile dunbari* Delo from the Devonian of Missouri (Bailey limestone). *O. dunbari* has the same number of both pygorachial and pygopleural segments as *O. formosa*; it has a similar deflection of the pygopleural segments, and a similar furrowing; the pygorachial segments have a similar arching of the posterior edge; and finally, the two species are of similar proportions. The cephalon and thorax of *O. dunbari* are unknown (see Delo, 1940, p. 56).

DETERMINATION OF DALMANITIDS.

In members of the Dalmanitidæ, the number of pygorachial segments is important both for generic and specific determinations. But the number of segments that can be counted varies with the maturity of the animal, and so it is very important to have a mature specimen on which to base a determination. Delo has pointed out that size is a helpful guide in making generic determinations, and it is also a specific character. Here again there is variation with stage of growth. It is therefore important in determining any of these forms to be sure that the trilobite is a mature specimen, otherwise the determination can be misleading. It is desirable to have a range of specimens in hand before a new species is described, and there is uncertainty, in my opinion, in describing a new species from a solitary pygidium as has been done.

The genus *Dalmanites* grades into the genus *Odontochile*, and difficulty can attach to their separation. However, most difficulties disappear if mature specimens are chosen, and then the criteria set out in the diagnoses of the genera objectively applied.

CHARACTER OF GENS.

The fact that for over 50 years so many species belonging to two genera have been given the one name indicates the solidarity of the gens. The forms are very much alike and constitute a closely related genetic sequence. The species described in this paper are apparently only some of a number belonging to the gens. Material seen from Tasmania, Victoria and New South Wales suggests the presence of other species. The gens is characterized by large eyes set high in the exoskeleton so as to rise well above the glabella. As far as it has been worked out, the genealogical relationships appear to be as follows:

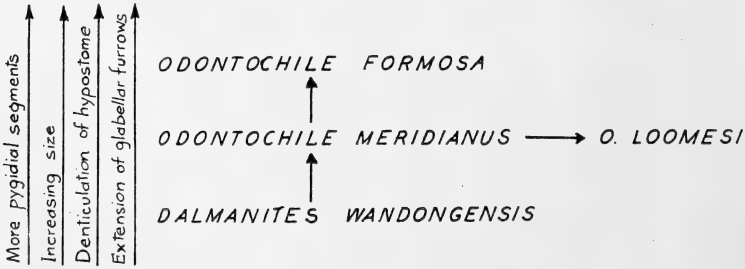

Fig. 1.

O. loomesi is very closely related to *O. meridianus*, but its different proportions from the other members of the gens shows that it is a branch away from the main line of development.

The signs of maturation in these trilobites are larger size, more advanced development of the posterior segments of the exoskeleton, greater tumidity, deeper impression of glabellar furrows, and in general a better development of the animal's exoskeletal structures. It is interesting to note that these same factors operate in the evolution of the gens. The only new structure in the sequence is the generic one of denticles on the hypostome—a minor specialization of an already existing part.

The glabellar furrows are of considerable phylogenetic significance, and their development in the gens is consequently of some interest and importance. In *D. wandongensis* the glabellar furrows do not reach the axial furrow. In the younger specimens of *O. formosa* (Pl. II, fig. 2), they reach nearer the axial furrow than they do in *D. wandongensis*, but still they do not reach it. In well-matured specimens of *O. formosa* like the holotype, however, the glabellar furrows do reach the axial furrow, although the part nearer the axial furrow is comparatively shallow. Nevertheless the glabellar furrows do definitely conjoin with the axial furrows. Thus in the life history of the individual *O. formosa*, the trend found in the gens as a whole is exemplified.

STRATIGRAPHICAL CONSIDERATIONS.

The genus *Dalmanites* was believed to be restricted to the Silurian until Delo found that in North America (though as far as is known not elsewhere in the world), there is a slight overlap into the Devonian. He has described forms from the Helderbergian. *Odontochile*, as far as is known, is restricted to the Devonian.

Odontochile formosa comes from beds which have been referred to the Lower Devonian. *Odontochile meridianus* and *O. loomesi*, on the other hand, come from beds which have been described by Dr. Ida Brown (1941) as Silurian in age. The range of *Odontochile* is therefore greater than formerly believed (as was the case with *Dalmanites*), or some revision of the age determination of the beds concerned is indicated. The beds with *Odontochile* also contain the genera *Pleurodictyum* (*vide* Hill, 1943, pp. 58–59) and *Dicranurus* (Gill, 1948), which are restricted to the Devonian elsewhere.

It should be noted that *Odontochile meridianus* and *O. loomesi* are not so well advanced in development as *O. formosa*, from which it may be inferred that they are older in age. A similar position was noted with *Dicranurus* (Gill, 1948).

Chapman (1914, p. 219) referred the beds on Broadhurst's Creek at Wandong to the Melbournian Series, but later (1915, p. 161, footnote) referred them to low down in the Yeringian or passage beds, making mention specifically of the presence of "*Dalmanites meridianus*". It was the presence of this fossil which influenced the reference of these beds to the Yeringian Series by the present writer in 1940 (p. 254). *Dalmanites* is a Silurian genus, but extends up into the Devonian (Helderbergian) in North America. *Dalmanites wandongensis* therefore does not determine the age of the beds at Broadhurst's Creek, Wandong. More palæontological work will have to be done before their place in the stratigraphic sequence can be established.

"*Dalmanites meridianus*" has been recorded from Killara (Gill, 1938, p. 170; 1939, p. 142). This is a species of *Odontochile*, but a determination is not attempted because the material in hand is not good enough for description. The same applies to specimens from Whittlesea (Chapman in Jutson, 1908), where the species also is an *Odontochile* (determined from F. S. Colliver Collection, No. 2784). Similarly, specimens from Tasmania (Etheridge, 1897) must await the collection of further material to effect their elucidation. The large number of pygorachial segments, a feature specially noted by Etheridge, again indicates the genus as being *Odontochile*.

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I am indebted to Mr. Harold Fletcher, palæontologist of the Australian Museum, Sydney, for information concerning New South Wales trilobite localities, and to Mr. Robert Withers, M.Sc., Dip.Ed., for similar information concerning the Kinglake trilobite. Mr. F. S. Colliver has made specimens available from his collection. Dr. Ida Brown kindly agreed to communicate this paper to the Society. The photographs were taken by Mr. L. A. Baillôt of the Melbourne Technical College, and Miss M. Johnson of the Geology Department of the University of Melbourne.

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EXPLANATION OF PLATES.

PLATE I.

Fig. 1.—*Dalmanites wandongensis*, sp. nov., internal cast of cephalon, *paratype*. Natural size.

Fig. 2.—*D. wandongensis*, sp. nov., internal cast of pygidium, *holotype*. Natural size.

Fig. 3.—*D. wandongensis*, sp. nov., eye of internal cast, ×4. *Paratype*.

Fig. 4.—*D. wandongensis*, sp. nov., eye of external mould, ×4. *Paratype*.

Fig. 5.—*Odontochile loomesi* (Mitchell), internal cast of complete carapace, *lectoholotype*.

Fig. 6.—*O. loomesi* (Mitchell), internal cast of eye, ×6. *Lectoholotype*.

PLATE II.

Fig. 1.—*Odontochile formosa*, sp. nov., internal cast of complete carapace, *holotype*. Natural size.

Fig. 2.—*O. formosa*, sp. nov., internal cast of cephalon of young specimen from Davies' Quarry, on the western branch of Stony Creek, about a mile north of Kinglake West State School (same locality as *Dicranurus kinglakensis*), *hypotype*. Natural size. Note that the second and third glabellar furrows fail to reach the axial furrows, as they do on the mature specimen. Univ. of Melbourne, Dept. of Geology, Reg. No. 1947.


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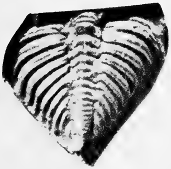
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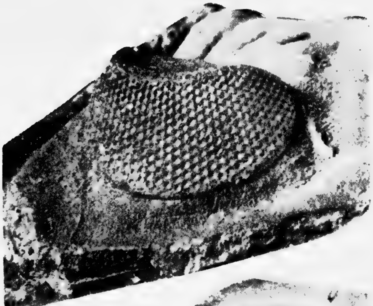
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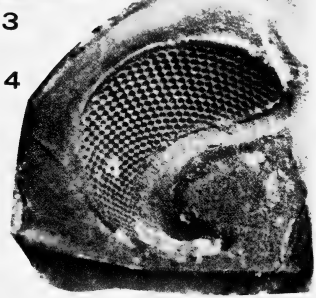
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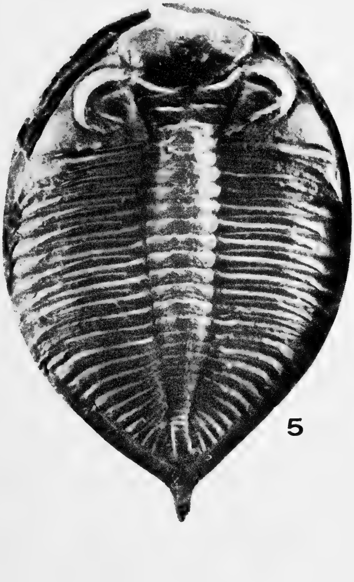
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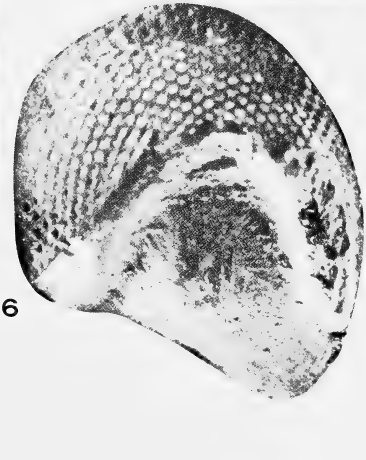
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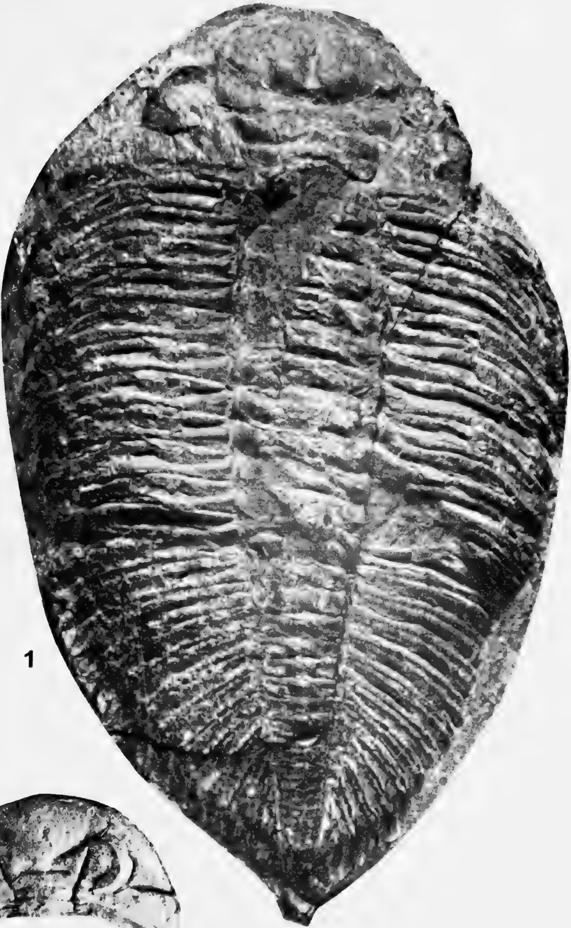

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OCCULTATIONS OBSERVED AT SYDNEY OBSERVATORY DURING 1947.

By W. H. ROBERTSON, B.Sc.

(Communicated by the GOVERNMENT ASTRONOMER.)

Manuscript received, January 6, 1948. Read (in title only), April 7, 1948.

The following observations of occultations were made at Sydney Observatory with the 11½-inch telescope. A tapping key was used to record the times on a chronograph. No correction was applied to the recorded times either for personal effect or to allow for error in the Moon's tabular longitude. The reduction elements were computed by the methods given in the Occultation Supplement to the *Nautical Almanac* for 1938 and the reduction completed by the method given there. The necessary data were taken from the *Nautical Almanac* for 1947, the Moon's right ascension and declination (hourly table) and parallax (semi-diurnal table) being interpolated therefrom.

Table I gives the observational material. The serial numbers follow on from those of the previous report (Robertson, 1947). The observers were H. W. Wood (W) and W. H. Robertson (R). In all cases the phase observed was disappearance at the dark limb. Table II gives the results of the reductions which were carried out in duplicate. The N.Z.C. numbers given are those of the new zodiacal catalogue (Robertson, 1940), as recorded in the *Nautical Almanac*.

TABLE I.

Serial No.	N.Z.C. No.	Mag.	Date.	U.T.	Observer.
				h m s	
141	219	5·1	Jan. 1	12 01 57·2	W
142	631	5·6	Jan. 4	12 35 57·7	W
143	742	6·0	Feb. 1	13 38 49·3	W
144	1169	5·4	Mar. 3	10 20 16·6	R
145	1263	7·1	Mar. 31	8 50 53·7	R
147	1270	6·1	Mar. 31	10 31 04·1	R
148	1274	5·7	Mar. 31	11 52 31·9	R
149	1279	6·4	Mar. 31	12 39 20·6	R
150	1233	5·8	Apr. 27	8 24 36·2	W
151	1365	6·1	Apr. 28	8 40 57·9	R
152	1689	5·5	May 28	9 17 59·8	R
153	2330	6·3	June 30	8 56 40·9	R
154	2337	6·4	June 30	10 44 16·1	R
155	1725	7·5	July 22	9 37 25·8	W
156	2430	7·0	July 28	11 27 07·5	R
157	2605	7·1	Sept. 22	8 57 48·2	R
158	2623	7·5	Sept. 22	12 34 58·6	W
159	2781	7·4	Sept. 23	13 56 20·5	W
160	2282	5·9	Oct. 17	9 43 21·9	R
161	2852	7·4	Oct. 21	9 30 40·4	W
162	3243	7·4	Oct. 24	13 10 03·7	R
163	3062	7·5	Nov. 19	9 58 01·8	W

TABLE II.

Serial No.	Lunation.	p	q	p^2	pq	q^2	Δσ	pΔσ	qΔσ	Coefficient of	
										Δα	Δδ
							″	″	″		
141	297	+ 93	+36	87	+34	13	−0·9	−0·8	−0·3	+10·3	+0·72
142	297	+ 83	−56	69	−46	31	−0·9	−0·7	+0·5	+13·2	−0·32
143	298	+ 99	−13	98	−13	2	+0·2	+0·2	0·0	+13·7	+0·07
144	299	+ 98	−18	97	−18	3	−1·2	−1·2	+0·2	+12·9	−0·29
145	300	+100	+ 1	100	+ 1	0	−1·1	−1·1	0·0	+13·4	−0·18
147	300	+ 54	−84	29	−45	71	−0·4	−0·2	+0·3	+ 5·0	−0·93
148	300	+ 97	−24	94	−23	6	+0·4	+0·4	−0·1	+12·4	−0·43
149	300	+ 96	+28	92	+27	8	−1·1	−1·1	−0·3	+13·6	+0·08
150	301	+ 75	+66	56	+50	44	−2·0	−1·5	−1·3	+11·4	+0·53
151	301	+ 20	−98	4	−20	96	−1·2	−0·2	+1·2	− 0·9	−1·00
152	302	+ 13	−99	2	−13	98	−0·4	−0·1	+0·4	− 4·5	−0·95
153	303	+ 99	−13	98	−13	2	−0·1	−0·1	0·0	+12·9	−0·39
154	303	+ 96	+29	92	+28	8	−1·4	−1·3	−0·4	+14·0	+0·02
155	304	+ 43	−90	18	−39	82	+1·8	+0·8	−1·6	− 0·1	−1·00
156	304	+ 71	+70	51	+50	49	−1·5	−1·1	−1·0	+11·5	+0·55
157	306	+ 97	−26	93	−25	7	0·0	0·0	0·0	+12·6	−0·33
158	306	+ 98	+20	96	+20	4	+1·2	+1·2	+0·2	+13·4	+0·14
159	306	+ 95	−32	90	−30	10	−1·0	−1·0	+0·3	+13·0	−0·27
160	307	+ 99	−17	97	−17	3	−0·8	−0·8	+0·1	+12·5	−0·45
161	307	+ 25	+97	6	+24	94	−0·6	−0·2	−0·6	+ 2·0	+0·99
162	307	+ 98	−20	96	−20	4	−1·2	−1·2	+0·2	+14·2	+0·16
163	308	+ 62	+78	39	+49	61	−0·6	−0·4	−0·5	+ 5·6	+0·92

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MICROMETRICAL MEASURES OF DOUBLE STARS.

by Harley Wood, M.Sc.

Manuscript received, December 11, 1947. Read (in title only), April 7, 1948.

The following measures were made with the 11½-inch equatorial telescope of Sydney Observatory. The stars were all observed with the telescope east of the pier and the hour angle was small in all cases except one recorded in the notes at the end. There are 210 measures of 71 stars. In the table columns 1, 2 and 3 give the star's name and C.P.D. number, and right ascension and declination (1900) from Innes' *Southern Double Star Catalogue*; 4, 5 and 6 respectively the date, position, angle and distance; 7 gives the magnification used, the position of the eyes parallel (. .) or perpendicular (:) to the position angle of the stars and the definition on a scale in which 5 represents perfection and 0 unworkability; 8 gives the difference in magnitude and 9 the number of nights for means.

Star	R.A.	Dec.	Date	p	d	M.E.D.	△m	
	h m	° ′	1900+	°	″			
β391	0 04·3	28 33	45·896	264·1	1·67	420. .2	0·1	
28°4			46·642	263·2	1·71	420. .3	0·0	
			46·766	265·6	1·63	420. .3	0·0	
			46·435	264·3	1·67		0·0	3n
h3447	1 31·5	30 25	46·642	104·8	1·55	420. .2	0·8	
30°186			46·766	108·3	1·47	420. .2	1·5	
			46·704	106·6	1·51		1·2	2n
△5	1 36·0	56 42	45·896	204·7	10·28	420 : 2	0·0	
56°329			45·918	204·9	10·31	250 : 2	0·1	
			45·937	204·9	10·49	250 : 1	0·1	
			45·967	204·8	10·49	250 : 2	0·0	
			45·929	204·8	10·39		0·0	4n
h3494	2 15·6	35 54	45·918	300·2	1·41	420. .3	0·1	1n
36°221								
h3494	(bis)		46·604	297·7	1·36	420. .3	0·1	
			46·648	295·7	1·42	420. .3	0·0	
			46·673	295·7	1·37	420. .4	0·1	
			46·675	295·9	1·36	420. .2	0·1	
			46·703	297·5	1·33	420. .3	0·2	
			46·727	296·9	1·42	420. .3	0·3	
			46·755	298·4	1·28	420. .2	0·2	
			46·766	297·1	1·35	420. .2	0·2	
			46·694	296·9	1·36		0·2	8n
Brs.1	2 39·8	25 55	45·937	191·1				
26°255			47·038	190·8	12·18	420 : 1	1·2	1n
△12	3 13·6	64 49	46·648	103·0	18·89	420. .3	1·7	
64°235			46·651	103·2	19·02	300. .2	2·2	
			46·650	103·1	18·96		2·0	2n

Star	R.A. h m	Dec. ° ′	Date 1900+	p °	d ″	M.E.D.	Δm	
△15	3 36·2	40 41	46·675	327·5	7·90	420 : 2	0·8	
40°343			46·703	327·6	7·77	420 : 3	0·6	
			46·727	327·7	7·79	420 : 3	0·8	
			46·702	327·6	8·82		0·7	3n
β1004	3 58·2	34 46	46·673	112·3	1·84	420. .4	0·5	
34°424			46·703	113·2	1·71	420. .3	0·3	
			46·727	113·7	1·84	420. .3	0·5	
			46·755	114·6	1·81	420. .2	0·5	
			46·714	113·4	1·80		0·4	4n
h3683	4 38·6	59 08	46·673	89·5	1·90	420. .4	0·1	
59°370			46·703	90·8	1·85	420. .3	0·1	
			46·727	89·9	2·05	420. .3	0·1	
			46·701	90·1	1·93		0·1	3n
△23	6 02·2	48 27	44·163	87·3	2·27	290. .2	0·4	
48°777			44·168	86·6	2·05	290. .3	0·5	
			44·166	87·0	2·16		0·4	2n
β755	6 31·9	36 42	44·168	256·9	1·54	290. .3	0·7	1n
36°1001								
Mlb2	8 03·3	60 06	44·223	351·4	1·66	520 : 2	0·5	
60°1056			44·226	350·0	1·63	520 : 2	0·3	
			44·302	353·8	1·85	290 : 2	0·5	
			44·250	351·7	1·71		0·4	3n
β208	8 34·8	22 19	44·215	206·7	2·14	520 : 2	1·5	
22°3752			44·226	208·0	2·09	520 : 2	0·8	
			44·278	207·5	1·98	520 : 4	1·0	
			44·240	207·4	2·07		1·1	3n
h4165	8 58·6	51 48	44·223	108·9	1·22	520. .2	1·0	
51°1821			44·278	110·0	1·15	520. .3	1·2	
			44·302	108·7	1·15	520. .3	0·8	
			44·271	109·2	1·17		1·0	3n
h4188	9 08·8	43 12	46·305	281·9	2·95	300. .2	0·3	
43°3450			47·272	282·9	2·82	420. .3	0·3	
			47·350	283·2	2·90	420. .2	0·1	
			46·975	282·7	2·89		0·2	3n
h4220	9 30·2	48 34	44·193	210·4	2·27	290 : 3	0·2	
48°2532			44·346	213·4	2·17	520 : 3	0·8	
			44·260	211·9	2·22		0·5	2n
L.Pl27	9 57·9	59 15	46·305	264·6	7·75	300. .2	2·5	
59°1638			47·363	266·7	7·70	420. .2	1·8	
			47·369	267·6	7·74	420. .2	2·2	
			47·012	266·3	7·73		2·2	3n
R141	10 17·2	66 40	44·302	45·1	2·17	520. .3	0·7	1n
66°1226								
R141	(bis)		47·272	43·1	1·93	420 : 3	0·8	
			47·355	44·0	1·86	420 : 2	0·7	
			47·369	45·3	1·93	420 : 2	0·8	
			47·332	44·1	1·91		0·8	3n
Brs5	11 20·4	61 06	44·346	203·0	2·54	520 : 3	1·5	
60°2911			44·431	202·9	2·51	290 : 3	1·5	
			44·450	201·7	2·57	520 : 2	1·5	
			44·409	202·5	2·54		1·5	3n

Star	R.A.	Dec.	Date	p	d	M.E.D.	Δm	
	h m	° ′	1900+	°	″			
Brs6 ..	.. 11 23·8	42 07	46·475	168·2	13·32	300 : 2	2·0	
41°5379			47·536	168·3	13·34	420. .1	1·2	
			47·006	168·2	13·33		1·6	2n
Hld114 ..	.. 11 50·0	55 32	46·442	181·6	3·10	300 : 1	0·1	
55°4711			46·461	181·6	3·10	300 : 1	0·1	
			46·475	182·8	2·92	300 : 4	0·2	
			46·459	182·0	3·04		0·1	3n
Rmk14 ..	.. 12 08·8	45 10	46·461	246·2	3·00	300. .4	0·8	
45°5842			46·475	246·0	3·15	300. .4	0·4	
			46·468	246·1	3·08		0·6	2n
Brs8 ..	.. 12 19·4	57 34	43·420	336·0	5·31	290 : 3	0·3	
57°5451			43·458	336·4	5·35	290 : 2	0·2	
			43·477	335·7	5·41	290 : 3	0·5	
			43·452	336·0	5·36		0·3	3n
Cor138 ..	.. 12 22·0	33 35	44·403	7·0	4·64	290 : 3	1·2	
33°3255			44·431	7·1	4·52	290 : 2	1·5	
			44·494	6·9	4·45	520 : 3	2·0	
			44·443	7·0	4·54		1·6	3n
R207 ..	.. 12 40·2	67 33	44·450	9·3	1·44	520 : 2	0·1	
67°2064			44·494	8·9	1·44	520 : 3	0·2	
			44·472	9·1	1·44		0·2	2n
Cor141 ..	.. 12 41·7	56 54	46·499	146·2	4·42	300 : 3	1·0	
56°5434			46·505	144·6	4·30	300 : 2	1·4	
			46·510	143·8	4·22	300 : 3	1·2	
			46·505	144·9	4·31		1·2	3n
Rmk16	.. 13 01·7	64 46	46·461	186·4	5·54	300 : 2	1·7	
64°2183			46·475	187·3	5·54	300 : 3	0·8	
			46·499	186·6	5·50	300 : 2	1·2	
			46·478	186·8	5·53		1·2	3n
Hrg86 ..	.. 13 25·8	61 50	46·510	240·6	1·86	420. .3	0·3	
61°3777			47·580	238·3	1·74	420 : 2	0·2	
			47·045	239·4	1·80		0·2	2n
HIII 101	.. 13 46·1	32 30	44·508	107·1	8·06	290. .2	0·7	
32°3512			44·518	106·2	8·10	290. .3	1·5	
			44·513	106·6	8·08		1·1	2n
β343 ..	.. 13 46·3	31 07	44·431	265·3	0·99	520. .2	0·4	1n
30°3752								
△151 ..	.. 13 50·7	55 33	43·477	45·2	23·29	290. .2	2·0	
55°5793+4			43·497	44·8	23·13	290 : 2	2·5	
			43·487	45·0	23·21		2·2	2n
Slr19 ..	.. 14 01·2	49 24	44·450	282·2	1·42	520. .3	0·1	
49°6679			44·494	283·2	1·30	520. .3	—0·1	
			44·518	285·4	1·44	520. .3	0·1	
			44·487	283·6	1·39		0·0	3n
Slr19 ..	.. (bis)		46·461	282·2	1·65	420. .2	0·0	
			46·475	284·4	1·59	420. .2	0·1	
			46·468	283·3	1·62		0·0	2n
h4687 ..	.. 14 29·5	36 07	45·565	98·5	1·58	290. .2	0·1	
36°6477			46·587	104·0	1·39	420. .4	0·1	
			46·076	101·2	1·48		0·1	2n

Star	R.A.	Dec.	Date	p	d	M.E.D.	Δm	
	h m	° ′	1900+	°	″			
α Cen	14 32·8	60 25	42·494	0·8	7·27	290 : 2	0·5	
			42·513	1·6	7·27	290 : 3	0·5	
			42·504	1·2	7·27		0·5	2n
△166	14 34·4	64 32	42·499	231·9	16·00	290. .2	4·0	
64°2977			43·477	231·9	15·72	290. .2	4·0	
			42·988	231·9	15·86		4·0	2n
h4707	14 45·8	66 00	44·494	51·7	0·94	520. .4	0·2	
65°2914			44·540	50·4	1·08	520. .3	0·1	
			44·518	51·0	1·01		0·2	2n
h4712	14 48·1	55 01	45·584	228·0	7·27	290. .1	0·8	
54°6214			46·461	228·3	7·19	300. .3	0·4	
			46·480	228·0	7·13	300 : 2	0·2	
			46·175	228·1	7·20		0·5	3n
h4728	14 58·3	46 40	42·499	73·6	1·84	290. .2	−0·1	
46°7178			43·554	77·5	1·85	290 ..2	0·1	
			43·026	75·6	1·84		0·0	2n
△179	15 07·8	43 01	44·590	45·7	10·60	290 : 3	1·5	1n
42°6963								
Hwe78	15 25·0	33 29	44·494	143·5	2·02	290 : 3	1·5	1n
33°3881								
h4788	15 29·0	44 37	42·513	0·5	2·51	290 : 3	3·5	
44°7483			42·551	2·4	2·49	290 : 3	2·5	
			42·532	1·4	2·50		3·0	2n
Hwe79	15 37·6	41 30	46·592	344·3	3·92	420 : 2	2·0	
41°7323			47·580	344·1	3·92	420 : 2	2·0	
			47·599	344·1	3·91	420 : 1	1·0	
			47·257	344·2	3·92		1·7	3n
Hld124	15 37·6	50 28	43·573	201·1	2·51	290 : 2	2·0	
50°8526			44·540	203·3	2·43	520 : 4	2·0	
			44·056	202·2	2·47		2·0	2n
Rmk20	15 38·8	65 08	45·603	149·2	2·28	290 : 2	0·1	
65°3139			45·617	148·9	2·11	290 : 2	0·1	
			45·610	149·0	2·20		0·1	2n
Cor193	16 01·1	37 46	46·480	91·1	4·15	300. .3	0·0	
37°6639			46·620	90·6	4·09	300. .2	0·0	
			47·613	92·0	3·89	420. .2	0·1	
			46·904	91·2	4·04		0·0	3n
Cor197	16 17·9	48 55	44·590	150·5	1·79	520 : 3	0·1	1n
48°8449								
Slr12	16 32·5	47 35	46·587	169·1	1·52	420 : 3	0·0	
47°7811			47·613	168·1	1·50	420 : 2	0·0	
			47·689	168·0	1·47	420. .2	0·1	
			47·695	168·5	1·45	420 : 2	0·1	
			47·396	168·4	1·48		0·0	4n
Cor198	16 33·3	47 28	43·573	97·2	2·75	290. .2	1·0	1n
47°7818								
Cor201	16 43·0	49 52	42·551	45·2	3·32	290. .3	0·1	
49°9629			42·581	41·2	3·05	290 : 3	0·1	
			43·554	44·8	3·10	290. .2	0·2	
			42·899	43·7	3·16		0·1	3n

Star	R.A.	Dec.	Date	p	d	M.E.D.	Δm	
	h m	° ′	1900+	°	″			
Brs13	17 11·5	46 32	42·590	214·7	4·84	290 : 3	4·0	
46°8513			42·595	214·5	4·75	290 : 4	4·0	
			42·592	214·6	4·80		4·0	2n
HIII 25	17 11·9	24 11	45·573	354·9	10·32	290 : 1	2·0	
24°5859			46·675	354·7	10·36	420 : 2	1·5	
			46·124	354·8	10·34		1·8	2n
h4949	17 19·5	45 45	42·672	256·5	2·46	290. .2	0·5	
45°8580			43·573	258·3	2·46	290. .3	0·5	
			43·122	257·4	2·46		0·5	2n
R303	17 36·9	54 06	44·590	106·6		290. .2	1·0	1n
54°8468								
Rmk22	17 48·9	55 22	42·595	90·9	2·54	290. .4	0·8	
55°8375			42·628	92·9	2·79	290. .2	1·5	
			42·612	91·9	2·66		1·2	2n
R306	17 51·2	36 00	47·613	17·9	3·67	420 : 2	2·0	
35°7563			47·719	18·8	3·71	420 : 4	3·0	
			47·728	17·9	3·74	210 : 1	3·0	
			47·687	17·2	3·71		2·7	3n
h5014	17 59·6	43 26	42·647	216·2	1·87	290 : 3	0·1	
43°8434			42·691	219·3	1·67	290. .2	0·1	
			42·669	217·8	1·77		0·1	2n
h5014	(bis)		46·587	214·2	1·78	420. .4	0·1	
			47·708	215·7	1·75	420 : 2	−0·1	
			47·722	215·4	1·65	420 : 3	−0·1	
			47·733	214·2	1·74	300 : 2	0·0	
			47·437	214·9	1·73		0·0	4n
h5027	18 05·5	54 23	45·666	138·0	15·05	290. .2	3·0	
54°8761			45·694	138·4	14·60	290 : 1	3·0	
			45·699	139·3	14·63	290 : 2	3·5	
			45·686	138·6	14·76		3·2	3n
h5034	18 08·8	46 03	47·613	99·1	2·58	420. .2	0·5	
46°9202			47·684	97·8	2·40	420. .3	0·5	
			47·689	100·9	2·52	420. .2	0·5	
			47·662	99·3	2·50		0·5	3n
Mlb5	18 24·1	66 21	42·653	293·4	4·83	290. .3	3·5	
66°3380			42·675	293·0	4·64	290. .2	3·5	
			42·664	293·2	4·74		3·5	2n
h5070	18 45·3	22 08	45·685	51·0	9·65	290. .2	0·1	
22°7218			47·708	52·7	9·34	420 : 2	0·1	
			47·719	51·2	9·60	420. .4	0·0	
			47·722	51·2	9·43	420. .3	0·0	
			47·208	51·5	9·50		0·0	4n
h5085	19 01·8	60 12	42·628	243·5	3·21	290 : 2	3·5	
60°7269			42·647	239·2	3·29	290. .3	3·0	
			42·638	241·4	3·25		3·2	2n
h5091	19 02·1	31 08	45·757	208·8	9·06	290 : 1	3·5	
31°5897			47·684	210·0	8·88	420 : 3	1·2	
			47·728	210·5	8·99	210 : 1	0·8	
			47·733	209·7	8·94	210 : 2	1·0	
			47·226	209·8	8·97		1·6	4n

Star	R.A.	Dec.	Date	p	d	M.E.D.	Δm	
	h m	° ′	1900+	°	″			
h5094	19 06·2	34 01	45·666	193·6	22·01	290 : 2	0·2	
34°8332			45·694	192·9	21·95	290 : 2	0·2	
			45·680	193·2	21·98		0·2	2n
h5117	19 21·2	44 05	45·666	261·5	6·23	290. .2	1·5	
44°9569			45·685	260·6	6·18	290. .2	2·0	
			45·732	260·8	6·07	290. .3	2·0	
			45·694	261·0	6·16		1·8	3n
h5140	19 40·4	65 09	42·653	83·7	1·93	290. .2	−0·1	
65°3825			42·710	82·4	2·05	290. .2	0·0	
			42·682	83·0	1·99		0·0	2n
h5163	19 56·2	63 20	45·688	251·1	1·52	520. .3	0·7	
63°4561			45·751	250·5	1·50	520. .3	0·7	
			45·720	250·8	1·51		0·7	2n
β763	20 17·1	42 45	45·688	233·9	1·15	520. .4	0·5	
42°9068			45·751	234·1	1·12	520. .3	0·8	
			45·720	234·0	1·14		0·6	2n
Jc18	20 27·1	40 54	42·724	224·6	4·79	290 : 2	0·7	
40°9315			42·762	225·0	4·38	290 : 3	0·5	
			42·743	224·8	4·58		0·6	2n
β153	20 41·4	26 47	47·719	265·5	1·64	420. .4	1·0	
26°7103			47·722	264·8	1·64	420. .3	2·0	
			47·881	267·9	1·64	420 : 2	2·0	
			47·774	266·1	1·64		1·7	3n
Rmk26	20 43·3	62 48	42·800	86·0	2·71	290. .2	0·2	
62°6180			45·732	87·2	2·67	290. .2	0·3	
			45·770	89·8	2·75	290. .2	0·1	
			44·767	87·7	2·71		0·2	3n
h5246	21 03·1	54 59	45·688	128·0	3·56	520. .4	0·1	
55°9530			45·795	129·3	3·58	290. .3	0·1	
			45·742	128·6	3·57		0·1	2n
Mlb6	21 20·6	42 59	45·732	147·0	2·97	290 : 2	2·0	
43°9451			45·751	146·2	3·01	290. .3	2·5	
			45·770	147·8	3·17	290 : 2	2·0	
			45·751	147·0	3·05		2·2	3n
λ466	21 59·0	40 11	45·803	259·9	2·05	520. .3	0·5	
40°9649			45·828	256·9	2·14	290. .2	1·0	
			45·816	258·4	2·10		0·8	2n
HN56	22 08·8	21 34	45·809	116·3	5·17	290. .1	1·0	
21°8078			46·862	114·7	5·21	300. .1	1·3	
			46·336	115·5	5·19		1·2	2n
I136	22 19·9	45 37	42·820	271·3	1·97	290. .2	1·0	1n
45°10295								
I304	22 40·9	48 50	45·770	357·8	4·63	290 : 2	1·5	
48°10811			45·795	360·0	4·45	290 : 3	1·5	
			45·782	358·9	4·54		1·5	2n
△246	23 01·5	50 14	42·820	256·4	8·76	290. .2	0·3	
51°11908			45·803	257·1	8·77	290. .2	0·2	
			44·312	256·8	8·76		0·2	2n

Star	R.A.	Dec.	Date	p	d	M.E.D.	△m	
	h m	° ′	1900+	°	″			
△247 ..	.. 23 12·1	61 33	45·809	288·9	45·50	290. .1	0·5	
61°6735+4			46·862	289·2	45·85	300. .1	0·5	
			46·336	289·0	45·68		0·5	2n
△251 ..	.. 23 34·1	47 12	45·828	274·7	4·17	290. .2	0·2	
47°10023			46·862	274·4	4·26	300. .2	0·2	
			47·881	274·4	4·00	420. .3	0·2	
			46·857	274·5	4·14		0·2	3n

Notes.

Star	R.A.	Date	
	h m		
β343 ..	.. 13 46·3	44·431	p presumably in error by 180°.
Slr19 ..	.. 14 01·2	44·494	p changed by 180°.
h4728 ..	.. 14 58·3	42·499	p changed by 180°.
h5014 ..	.. 17 59·6	47·708 and 47·722	p changed by 180°.
β153 ..	.. 20 41·4	47·881	measured at hour angle +2·1h.

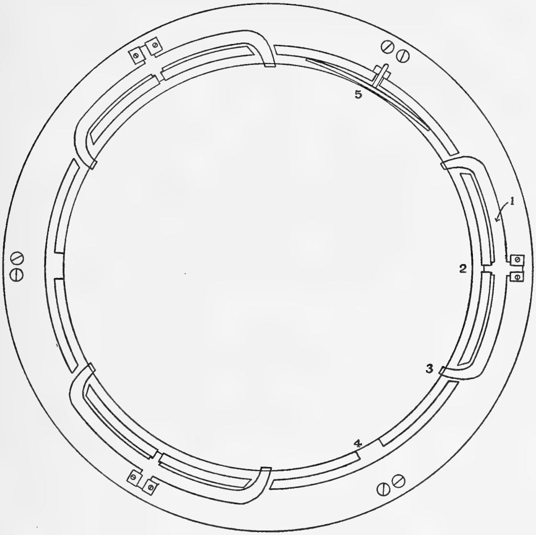
A CELL FOR AN 11½-INCH LENS.

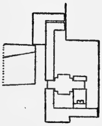
By Harley Wood, M.Sc.

Manuscript received, January 6, 1948. Read (in title only), April 7, 1948.

The 11½-inch equatorial telescope was purchased for observation of the transit of Venus in 1874. The performance of the lens has never been really satisfactory and several attempts have been made to improve it (e.g. Russell, 1878). The lens, of the Fraunhofer type, has been subject to trouble arising from flexure. It was supported at three points and the crown lens was separated from the flint by three pieces of foil just of sufficient thickness to prevent contact of the components at the centre. On nights of good seeing the central discs of star images viewed through the lens were distinctly triangular and the diffraction rings either at the focus or extrafocal showed the same feature. The position angles of the vertices of the triangle remained the same relative to the points of support irrespective of the orientation of the components in the cell. In some positions of the crown on the flint there is a conspicuous astigmatism. It was with the idea of removing the effects of flexure that the lens mounting described below was designed. With the lens in the new cell and the relative positioning of the crown and flint arranged to reduce to a minimum the astigmatism which has been mentioned the performance of the lens is much improved and the triangularity of the diffraction pattern has disappeared. Previously there was some fear that the character of the images might give rise to systematic error in fine micrometric work such as the measurement of double stars, but no such feeling exists with the new arrangement.

In the figure the innermost circle represents the lens supported at six points round its circumference on the tips, 3, of three levers, 1, pivoted at 2. The lateral support of the lens consists of two fixed arcs, 4, and a spring, 5, capable of maintaining a pressure of fifteen pounds, approximately equal to the weight of the lens. A screw is fastened to the back of this so that it may be pulled back slightly to enable the lens to be placed in or removed from the cell. The spring, lined with velvet, has a ridge along the back which enables it to rock on the cell wall, so that when released it presses on the side of both components of the lens. The cell is attached to the telescope by three screws and three pushing screws are provided to enable it to be squared accurately on to the end of the telescope. The smaller figures below the main one give radial sections through the cell at the points marked 2, 3 and 4 and show the pivot, the lever projecting under the lens and the fixed lateral support. Also shown in these drawings is the light metal covering, which excludes dust from the lever system and the interior of the telescope, and the ring in the top of the cell which retains the lens. The ring is cut away except at three points round the cell near the pivots and is adjusted by three pairs of screws so that it just fails to be in contact with the crown component. The crown component is now separated from the flint by three solid metal leaves (0·28 mm. thick) and three thin springs placed alternately around the lens at points corresponding to those where the flint is supported on the lever system. The springs are honed down so that each supports approximately one-sixth of the weight of the crown. The cell was made by E. W. Esdaile.

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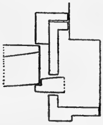
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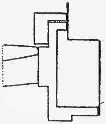
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This way of mounting lenses should be useful for much larger sizes. In cases where the two components of a lens were separated the lower one might be supported by a double-ended lever system like this one and the upper one made more readily adjustable relative to the lower by using three weighted levers and three adjustable points of support.

REFERENCE.

Russell, H. C., 1878. This Journal, **12**, 247.

THE PARACLOACAL (ANAL) GLANDS OF *TRICHOSURUS VULPECULA*

By A. BOLLIGER
and W. K. WHITTEN.*
From the Gordon Craig Research Laboratory, Department of Surgery, University of Sydney.

With Plates III-VI.

Manuscript received, March 1, 1948. Read, April 7, 1948.

William Cowper (1704), who gave the world the first description of the urogenital tract of a male marsupial (*Didelphys virginiana*), made the following statement in describing the muscles on the lower abdomen :

> " Immediately under the skin about the cloaca I found a thin fleshy muscle enclosing the preputium and lower part of the rectum and odoriferous bags, together with four mucous glands at the root of the penis . . . "

These odoriferous bags no doubt refer to all or some of the glands which subsequently were called anal glands,† a name apparently used for the first time by Daubenton (*ca.* 1750), who mentioned the occurrence of a pair of anal glands in *Didelphys virginiana*. Subsequently these glands were noted in marsupials by Carus (1840), Michel St. Ange (1856), Garrod, Brass (1880), Widersheim (1893), Eggeling (1893), Disselhorst (1897), Hill (1899) in a wide variety of marsupials as pointed out by Van den Broek (1904). This last-named author gave us a detailed description of these glands referred to by him as rectal glands of the female of *Halmaturus* sp., *Petrogale penicillata*, *Cuscus orientalis* and *Sminthopsis crassicaudata*. He summarized his findings as follows :

On both sides of the lower part of the rectum and the cloaca are present three types of glands :

1. Tubular cloacal glands, which are branched tubular glands lined by simple cylindrical epithelium. They occur in the wall of the cloaca and in some species even higher up in the rectum and urogenital canal.
2. Hair follicle glands, which are complex branched sebaceous glands.
3. Rectal glands (anal glands). One pair only of these extraordinarily developed modified sebaceous glands occur. They are cell-producing structures but the secretion does not liquefy as in ordinary sebaceous glands.

In 1910 Van den Broek briefly referred to the rectal glands of male marsupials, particularly *Hypsiprimnus*, and classified these structures as accessory sex organs but adhered strictly to the term rectal glands. He stated on this occasion that they occurred in two pairs, of which in some species only the caudally situated pair developed.

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* Research Officer employed by the Council of Scientific and Industrial Research.

† As far as we are aware, previously no other author has referred to Cowper's observation in connection with these glands.

The work of Van den Broek suffered from the disadvantage that in Holland he usually had at his disposal one specimen only of each species examined. These specimens were sometimes unsatisfactorily preserved. This led to certain anatomical inconsistencies and no physiological aspects could be studied.

In spite of these drawbacks and the necessary incompleteness of Van den Broek's work executed some forty years ago, no further detailed account on the glands has been published since. McKenzie (1919), in his monograph on the urogenital tract of marsupials, referred to two sebaceous glands in the rectal region of *Trichosurus vulpecula* and also to a pair of ductless sex glands. Schaffer planned an extensive investigation on anal and related glands in general. However, only an introductory article on the history of the subject (1924) and some small references in an article on skin glands (1925) have been published as far as can be ascertained. Schaffer (1925) proposed the term paraproctal glands for these structures.

In the urine of *Trichosurus vulpecula*, Bolliger and Whitten (1940) observed spherical refractile bodies which subsequently were shown to originate from some of these glands. This observation led to the present study of these structures, which shall be referred to as paracloacal glands. They will be further subdivided into (*a*) scent or oil secreting, and (*b*) cell secreting glands, and an attempt shall be made to clarify in at least one species, *Trichosurus vulpecula*, the anatomical and functional position of these glands which may well be considered a marsupialian characteristic.

EXPERIMENTAL.

Forty living specimens of *Trichosurus vulpecula*, the common Australian phalanger or possum, of both sexes and different ages were examined. The paracloacal glands were palpated and their contents repeatedly expressed. The urine of these animals was also investigated. About 20 of these animals were killed or died and the glands were examined macroscopically and microscopically. The sections were stained with hæmatoxylin and eosin and with Sudan IV (Fett Ponceau).

In addition, glands of this nature were examined in living and dead specimens of *Pseudocheirus laniginosus*, *Macropus robustus*, *Petaurus papuanus* and *Perameles nasuta*.

FINDINGS.

(*a*) *The Scent or Oil Secreting Glands.*

I. Morphology.

Macroscopic: In *Trichosurus vulpecula* of both sexes a pair of egg-shaped glands about 0·5–1·5 cms. long and weighing about 0·4–1·5 gms. in the adult lie obliquely along the lateral walls of the rectum, with the larger end caudad and with the inferior extremity attached to the rectal wall by means of fibrous tissue. These glands can readily be palpated in the living specimen and are easily movable over the caudal rim of the pelvis about 1 cm. from the pubic symphysis. They are larger in males than in females. Each gland is a hollow viscus, the wall of which is 1–2 mms. thick. It floats on water.

A fine duct leaves each of these glands on the mesial inferior aspect and passing caudally penetrates the cloacal wall and opens into the interior of that organ about 2–3 mms. from the cloacal rim. (Plate III and Plate IV, Fig. 1.)

Microscopic: The gland wall consists of the following layers: (1) The secreting epithelial layer, (2) a lamina propria, and (3) a muscular tunic. (Plate IV, Fig. 2.)

The epithelial layer is thrown into many folds. The major folds are subdivided into smaller folds. The number of folds varies considerably in different animals and also depends to some degree on the distention of the gland cavity. The epithelium is several cells thick and consists of large cuboidal or polygonal cells. The cytoplasm of these cells is granular and stains pink with eosin. In some instances the cytoplasm is foamy in appearance. Many of these foamy cells are seen in different stages of disintegration. The nuclei are round and have a well defined membrane and a nucleolus. Particularly in the cells with foamy cytoplasms the nuclei are frequently pyknotic and crenated or are completely absent. (Plate V, Fig. 1.) These cells separate from the epithelium and disintegrate to form a secretion consisting of oil droplets of relatively uniform size dispersed in a small amount of aqueous medium.

On staining frozen sections with Sudan IV nearly all the epithelial cells close to the lumen are covered with strongly red staining granules. The lamina propria is sparse, and adjacent to the muscular layer contains cavities with single columnar epithelial lining which resemble ducts of sweat glands.

The muscular coat consists of a few circular bundles which are greatly reinforced by longitudinal fibres on one of the lateral surfaces. These fibres are striated (voluntary muscle).

II. Physiology.

(*a*) *Secretions from the Scent or Oil Producing Glands.* The contents of the oil producing glands consist of a cream coloured oily liquid (about 0·5–1·0 ml.) which has an unpleasant odour resembling that of rotten onions or garlic. On microscopic examination this liquid is found to consist of oily droplets emulsified in an aqueous phase. On drying this emulsion in the desiccator a white semi-solid stays behind. This substance though not soluble in water is markedly hygroscopic and gives a strongly positive Burchhardt-Liebermann reaction indicating the presence of cholesterol or cholesterol esters. The nature of the contents of these glands may therefore be well considered as some form of sebum which is ultimately secreted from the gland through a fine duct whose opening is about 2 mms. from the cloacal rim. Frequently this secretion can be demonstrated on the intact animal by pressing on the oil-producing gland. The creamy secretion with its characteristic odour can be seen appearing on the orifice of the duct and recognised by its odour. The administration of adrenalin or pilocarpin did not bring on a secretion. However, in handling certain animals and in the ensuing struggle secretion frequently occurs and can be obtained from the orifice near the cloacal rim. These animals usually empty their bladder on this occasion and the secretion is detected in the urine by its strong odour. On the other hand, no secretion can be obtained from the oil-producing gland from many struggling animals or even by pressing on the gland, though the typical secretion can still be aspirated from the glands directly by puncturing the wall with a fine hypodermic needle. In these instances it appears as though the narrow duct were blocked, perhaps by inspissated secretion. In animals dying rather suddenly as, for example, after the administration of an overdose of an anæsthetic, a copious secretion from the oil glands nearly always occurs. If dying slowly from disease, this secretion does not occur.

(*b*) *The Effect of the Surgical Removal of the Scent Glands.* The scent glands can be readily amputated through a skin incision and in consequence no further secretion from the ducts is noticed. After observing two animals for over six months, no irregularities in defæcation were noticed and the general health of the animals did not suffer from this operation. The glands did not reform from the unexcised ducts.

(*b*) *The Cell Secreting Glands.*

I. Morphology.

Macroscopic: Caudally but very close to the scent glands another pair of glands occurs in both sexes which is palpable on the lateral wall of the cloaca about 1 cm. from the external orifice just beneath the mucosa. They are firmly attached to the surrounding tissue. These bodies are spherical or heart-shaped and usually are bi-lobed, though in two specimens they were found to contain three lobes. One gland of one animal consisted of one lobe only. In all cases, however, the lobes are enclosed by a common capsule, the outline of which indicates the subdivisions of the enclosed gland. In contrast to the scent glands these glands do not float on water. Each lobe of these glands is provided with a duct about 1 cm. long which traverses the cloacal wall obliquely to open on each side of the duct of the oil producing gland and about 1 mm. from it. These two or three fine ducts are often remarkably pigmented and almost black at the orifice. Thus we usually find on the lateral aspects of the cloacal wall three ducts parallel to each other and opening about 0·2 cm. above the external orifice of the cloaca. The central opening which is from the scent gland is not or is only slightly pigmented and more difficult to see. (Plate III and Plate IV, Fig. 1.)

Microscopic: The wall of each lobe of the cell producing gland also consists of three elements: (1) the secreting epithelial layer, (2) a lamina propria, and (3) a muscular tunic.

Superficially, the secreting epithelial layer has a somewhat similar appearance to that of the scent gland, but is usually thicker, leaving less unoccupied space in the interior of the glands. (Plate V, Fig. 2).

The large pink staining polygonal cells (30μ diam.) also have a granular cytoplasm which may become quite foamy in appearance in the cells nearer the surface. Furthermore, some cells on the surface of the epithelium are ovoid in shape and with a cytoplasm consisting of only a fine reticulum. On the other hand, the cell membranes of these apparently dying cells are thickened, sharply defined and refractile. (Plate VI, Fig. 1.) These cells are encountered in the interior of the glands, in and at the orifices of the pigmented ducts and ultimately in the urine. (Plate VI, Fig. 2.) As in the scent glands, the cell nuclei are round in general, have a well-defined membrane, and a nucleolus. Some nuclei in the faintly staining foamy cells with a well-defined membrane are pyknotic and crenated, but they are frequently still present when the cell has separated from the epithelium. Subsequently, these nuclei disappear.

The interior of a number of these cells just before or after being cast off from the epithelium contains large granules which stain red with Sudan IV. All the other epithelial cells, however, possess only small and faintly fat staining granules. The cast off cells obtained in the secretion of the ducts or in the urine practically always contain fat droplets covering the greater part of the cell and staining strongly with Sudan and Osmium. In the unstained specimen these fat droplets frequently give the cell the appearance of a parasitic ovum.

The lamina propria is better developed than in the oil glands. In addition to a thin layer of muscle surrounding the whole gland each lobe has its own muscular layer which frequently becomes very pronounced between adjacent lobes.

Tubules lined with a single columnar epithelium which resemble ducts of sweat glands are seen in the muscular layer close to the epithelium.

II. Physiology.

As pointed out previously, the desquamated cells from the cell producing glands do not liquefy and form the major part of a secretion consisting of these cells suspended in a small volume of an aqueous medium. This secretion unlike that of the scent gland has no marked odour. It passes down the two ducts from each gland and becomes deposited inside the cloaca but very close to its rim, and whenever the animal urinates it is washed away with the stream and is practically always found in the urine.

These cells remain intact for several weeks even if the urine putrefies. They have been observed in the urine of the young *Trichosurus vulpecula* as soon as it leaves the pouch of the mother, and generally speaking they are present in exceptionally large amounts in immature animals of both sexes, viz. 5–20 cells in a dry low power field. In adult specimens they are more numerous in males than in females. In females they can sometimes only be found after examining many fields or in the centrifuged sediment.

On defæcation the appearance of cell and oil gland secretion may be seen because the rim of the cloaca becomes sufficiently everted to allow the orifices of the ducts to open externally. On this occasion these secretions may be deposited on the fæces.

The Effect of the Surgical Removal of the Cell Producing Glands. Through a skin incision the cell producing glands (which are firmly attached to the surrounding tissues) can be dissected out quite readily. No further secretion typical of these glands can be noticed for several months. After about six months, however, signs of testicular degeneration were noted in several animals, but it is felt that the number of experiments is too small as yet to draw any definite conclusions.

Other Marsupials Examined.

Macropus robustus (Kangaroo).

On a formalin preserved specimen (male) the findings of Van den Broek were confirmed in that only one pair of glands were present and the duct which is 2 to 3 cms. long, opens into the rectum about 1 cm. from the cloaca. The cloaca, however, differs from that of the other species examined in that it is sparsely provided with hairs.

Perameles nasuta (Bandicoot).

In the bandicoot also only one pair of glands was found. These glands produced a cellular secretion and their ducts opened within 1 mm. of the dorsolateral margin of the cloaca. The cloaca was similar to that of *Trichosurus vulpecula* and *Pseudocheirus laniginosus* in that it was without hairs.

Pseudocheirus laniginosus (Ring-tailed Possum).

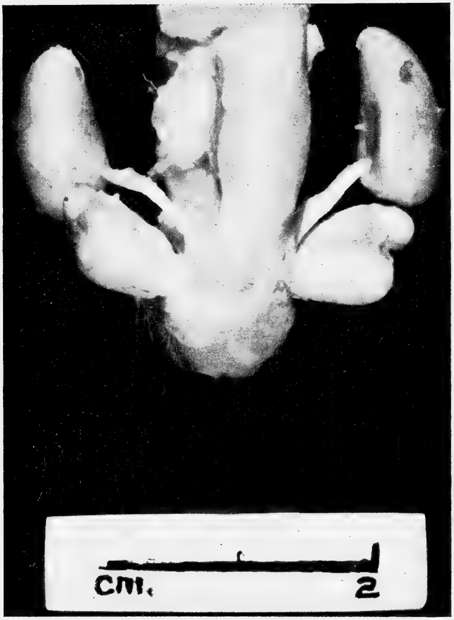
There are two pairs of glands, as in *Trichosurus vulpecula*, but both produce an oily secretion without any cellular elements.

Petaurus papuanus (New Guinea Flying Phalanger).

Two pairs of paracloacal glands could be palpated in the living animal, but only oily droplets and no typical cell gland bodies could be found in the urine.

DISCUSSION.

The anatomy of the hind end of marsupials is different from that of higher mammals and this makes it difficult to label the glands situated in the characteristic conically shaped cloacal hillock in terms of general mammalian anatomy. They have variously been called rectal, anal and paraproctal glands by different authors. All these terms, however, imply that these glands are connected with the lower end of the intestinal tract. However, this assumption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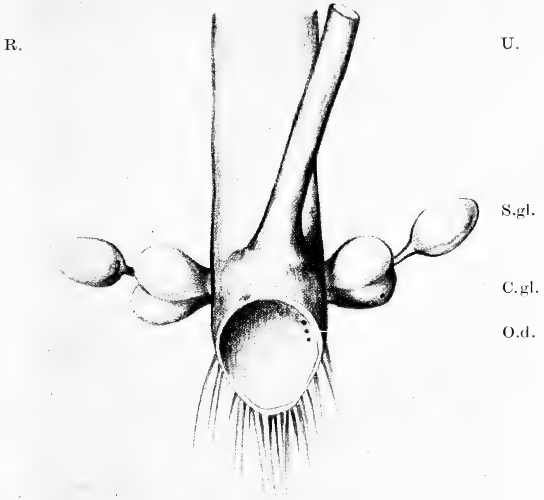

Fig. 1.

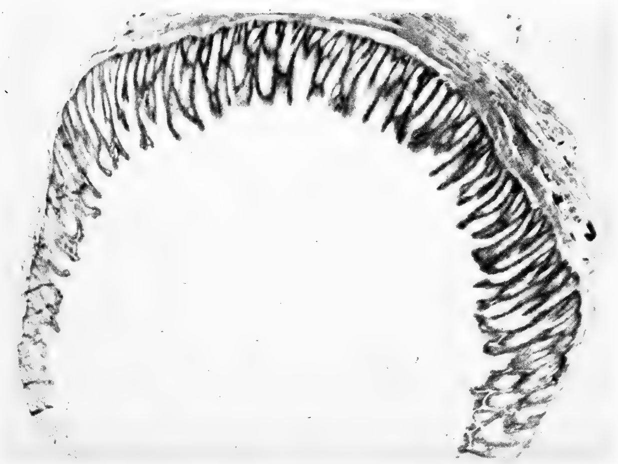

Fig. 2.

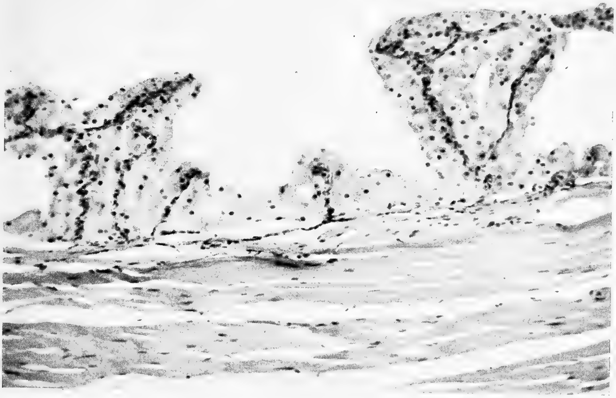

Fig. 1.

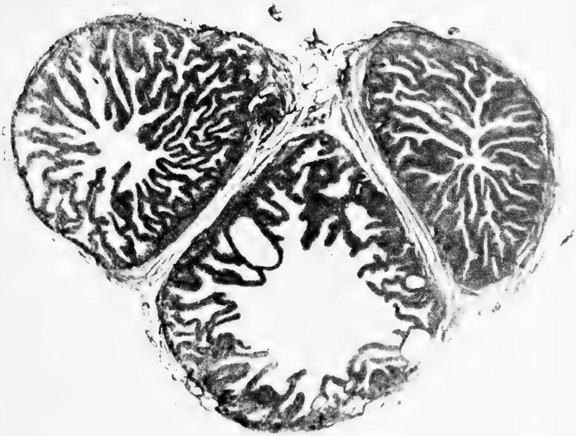

Fig. 2.

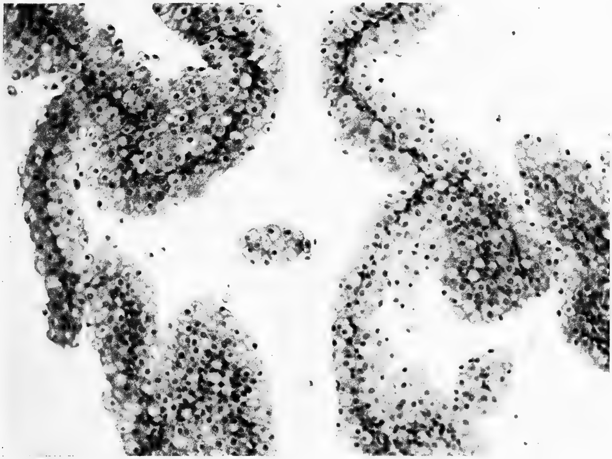

Fig. 1.

Fig. 2.

has not yet been proven in any way and the possibility that some of these glands may for example correspond to the prepucial glands of eutherian mammals cannot be wholly excluded. Therefore, it was decided to name them paracloacal glands, a non-committal term. It is realized, however, that some of the fully grown marsupials do not possess a cloaca, as for example *Didelphys virginiana*, where the ducts of at least one pair of these glands open exteriorly besides the anal rim. The new terms " cell and oil producing glands " are self-explanatory (though somewhat clumsy).

Originally Van den Broek (1904) recognized only one pair of these glands as true rectal glands, the specific term used by this author for what we term paracloacal glands. In a subsequent publication (1910) dealing with the structure of the male reproductive organs he postulated the occurrence of two pairs of rectal glands in marsupials, but only one pair may develop fully, as in the case of *Macropus* sp. However, he also states that the occurrence of one pair of glands is a characteristic of Phalangeridæ, which in this paper is shown to be incorrect in the case of both sexes of *Trichosurus vulpecula* and *Pseudocheirus laniginosus*. Only on one occasion we found a phalanger which presented a single pair of fully developed glands. These glands were of a peculiar structure and could not be classified definitely as either cell or oil glands. The specific pair of " rectal " glands, by Van den Broek's original definition, corresponds to the cell producing glands as described by us in detail in *Trichosurus vulpecula*. The Dutch author described them as extraordinarily well developed and modified sebaceous glands. In his sections of these structures he noticed that the cells secreted by them do not liquefy as in ordinary sebaceous glands, and he expressed the opinion that the purpose of these glands consisted in lubricating the terminal section of the rectum and cloaca in order to facilitate the passage of the fæcal bolus.

Our investigations on *Trichosurus vulpecula* confirmed the cell producing function of these glands. They further brought out the fact that these cells are secreted fairly continuously and are washed away from the cloacal wall by the urinary stream and are found in the urine. It is these cells from the cell producing glands which give the urinary sediment of *Trichosurus vulpecula* and certain other marsupials, these characteristic bodies frequently resembling ova of parasites and whose nature is now explained for the first time.

In the case of the possum it is hardly feasible to assume that this cellular secretion has a lubricating action in the process of defæcation because before the fæces leaves the extended anus it is in no way in contact with the openings of the ducts from these glands. The as yet unexplained nature of the cell producing glands has been studied by removal and endocrine experiments which seem to indicate that these structures respond as if they were accessory sex glands and probably also necessary for gonad maintenance.

The fact that the cells of the cell producing gland do not liquefy as they usually do in sebaceous glands might have an analogy in the prepucial glands of an eutherian mammal, the weasel (*Putorius nivalis*), in which the lining also consists of a stratified epithelium whose surface cells are detached and secreted as such (Schaffer, 1925). However, it has to be pointed out that these prepucial glands are without ducts and open directly on to the surface of the fold. Nevertheless, the papillæ and crypts of these glands closely resemble those of the paracloacal glands.

On the basis of Van den Broek's findings Schaeffer (1925) suggests that these holocrine glands arise from definite epidermal areas which have been detached from the surface of the body and become located subcutaneously in the modified form of large encapsulated gland bodies with long ducts. The epidermal nature is demonstrated by the high papillæ which project into the broad squamous epithelium of the gland. This conception is supported by the observation that typical sweat gland structures are found in the walls of these glands. Van den Broek (1904) apparently referred to these structures as tubular cloacal glands. The continuous desquamation of cells may be considered a further epidermal characteristic.

In spite of a superficial similarity the scent or oil producing glands differ histologically from the neighbouring cell glands and in *Trichosurus vulpecula* a definite functional difference lies in the fact that the cells secreted liquefy and the liquid secretion formed has an unpleasant odour. This property seems to place the scent glands of *Trichosurus vulpecula* and other marsupials amongst the scent glands met with in many species of mammals in general. They appear to be definitely related to the defence of the animal and they also may play a rôle in the sex behaviour.

SUMMARY.

The large glands in the subcutaneous tissue of the cloacal hillock of *Trichosurus vulpecula* and other marsupials have been examined anatomically and physiologically. They are referred to as paracloacal glands.

The two pairs present in both sexes of *Trichosurus vulpecula* have been subdivided according to their activity into a pair of oil producing or scent glands and a pair of cell producing glands.

The individual oil producing gland is a single hollow viscus. Its main function seems to be that of a scent gland.

The cell producing gland is usually a bilobed or trilobed structure. Its function remains obscure. These glands do not liquefy their cellular secretion which ultimately appears in the urine as cells. This phenomenon has so far not been encountered in eutherian mammals.

Histologically all these glands are of a sebaceous nature. However, definite differences exist between the epithelial layers of the two glands.

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EXPLANATION OF PLATES.

PLATE III.

Dissection illustrating the egg-shaped scent glands and the bi-lobed cell-producing glands in a male *Trichosurus vulpecula*. Note the ducts from the scent glands entering the wall of the cloaca close to the caudal end of the cell-producing glands. The material for this dissection was hardened in formalin. Posterior aspect.

PLATE IV.

Fig. 1.—Semidiagrammatic drawing from freshly dissected material illustrating the scent and cell-producing glands of a female *Trichosurus vulpecula*. Anterior view. In order to show the relationship between the orifices of the ducts and the rim of the claoca the cloacal opening is depicted in a distended state.

R. = rectum. U. = Urogenital canal. S.gl. = Scent gland. C.gl. = Cell-producing gland. O.d. = Orifices of ducts.

Fig. 2.—Cross section of part of the scent or oil-producing gland obtained from fully grown male *Trichosurus vulpecula*. The photograph demonstrates the folded epithelium and the reinforced muscular layer on one of the lateral surfaces. (× 6.) Stained with hæmatocylin and eosin.

PLATE V.

Fig. 1.—Epithelial layer and *lamina propria* of scent gland. Note the cuboidal or polygonal cells and their nuclei. (×100.) Stained with hæmatoxylin and eosin.

Fig. 2.—Cross section through a trilobed cell-producing gland obtained from a female *Trichosurus vulpecula,* who had received injections of testosterone. The strongly developed epithelium resembles that of a normal male. (×6.) Stained with hæmatoxylin and eosin.

PLATE VI.

Fig. 1.—Microphotograph of some of the papillæ of the cell-producing gland epitheilum. Note the well defined membrane of the dying cells. (×100.) Stained with hæmatoxylin and eosin.

Fig. 2.—Cellular secretion from the cell-producing glands of a fully grown female *Trichosurus vulpecula.* The specimen which was obtained from the orifices of the ducts is unstained. It has, however, been diluted with water in order to obtain individual cells. (×400.)

A SURVEY OF ANTHOCYANINS IN THE AUSTRALIAN FLORA.

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Contents.

Introduction.

The synthetical work on the anthocyanin pigments by Robinson and his school led to the development of methods of identification of individual anthocyanins in solution in plant extracts (Robinson and Robinson, 1931, 1932, 1933, 1934 ; Lawrence, Price, Robinson and Robinson, 1938). The relative ease of identification has made possible large-scale surveys of the distribution of anthocyanins in plants, and particularly in flowers (Lawrence, Price, Robinson and Robinson, 1939 ; Taylor, 1940 ; Beale, Price and Sturgess, 1941), which have had as their main objective the elucidation of the biosynthesis of the anthocyanins. Genetical investigations bearing on this and other problems have also been facilitated (Scott-Moncrieff, 1939 ; Beale, 1941). The information collected in the surveys may in addition have some value to phylogenetics.

A large proportion, probably the majority, of the plants examined in these surveys had been cultivated in gardens for many years and it may be expected that the distribution of anthocyanins in such plants is affected by artificial selection, preservation of mutant forms and hybridisation. We have therefore carried out a survey of the occurrence of anthocyanins in the flowers of some 300 native Australian species, including some tropical species from New Guinea, together with a smaller number of fruits. Approximately 20% of the species investigated were cultivated, and the results for these have been analysed separately. All available anthocyanin-containing species, both wild and cultivated, were examined irrespective of size or colour.

The list of species examined is set out in Table 1. As in previous surveys, the botanical classification used is that of Hutchinson (1926), arranged in reverse order so that the more highly developed plants are placed first.

TABLE 1.

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.

(i) Mode of occurrence of anthocyanin in the flower or fruit.
(ii) Colour of anthocyanin in the flower or fruit.
(iii) Anthocyanidin.
(iv) Glycoside type.
(v) Distribution of the species along the east coast of Australia (or New Guinea or Western Australian species).

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.					
LAMIALES.					
LABIATÆ (76–264).					
Ajuga australis R.Br. ..	A†	Blue	Delph.	PG.	G.
Hemigenia purpurea R.Br.	A	Red/Blue	Delph.	Dimon.	33/36
Plectranthus parviflorus Henck.	A	Red/Blue	Cyan.	Dimon.-A	G.
Prunella vulgaris Linn. ..	A†	Red/Blue	Malv. (Fe+)	PG.	ST/Tm.
Prostanthera lasiantha Labill.	Bb	Red/Blue	Malv.	Digly.	ST/Tm.
P. linearis R.Br.	A	Blue	Delph.	Dimon.	ST.
P. ovalifolia R.Br. ..	A*	Blue	Malv. X	(Note 11)	ST.
P. Sieberi Benth. ..	A*	Blue	Cyan.	Bios.	33/36
P. sp.	A	Blue	Malv. X	Dimon.	
Westringia rosmariniformis Sm.	Bc	Red/Blue	Malv.	Digly.	ST/Tm.
VERBENACEÆ (76–263).					
Clerodendron tomentosum R.Br.	Calyces	Red	Peon.	A-sugar	Tr/ST.
C. sp.	A	Red	Pel.	Bios.	NG.
Duranta Plumieri Jacq. ..	A	Red/Blue	Malv.	Mon.	NG.
Faradaya sp.	A	Red	Peon.	Mon.	NG.
Premna integrifolia Linn.	Fruit	Blue/Black	Malv.	Mixture	NG.
Stachytarpheta dichotoma Vahl.	A	Blue	Malv.	Digly.	NG.
PERSONALES.					
ACANTHACEÆ (75–259).					
Eranthemum variabile R.Br.	A†	Blue	Malv.	PG. ?	Tr/ST.
Graptophyllum Earlii F. Muell..	A*	Red	Pel.	Mon.	Tr.
BIGNONIACEÆ (75–257).					
Tecoma australis R.Br.	Bb	Red	Cyan. + Peon.	PG.	G.
Tecomanthe dendrophilia K. Schum.	A	Red	Malv.	Mon.	NG.
Unidentified sp.	Bb	Red/Blue	Cyan.	Bios. ?	NG.
LENTIBULARIACEÆ (75–254).					
Utricularia dichotoma Labill.	A	Red/Blue	Delph.	Dimon.	ST/Tm.
SCROPHULARIACEÆ (75–252).					
Veronica Derwentia Littlej.	A†	Blue	Nitrogenous ?	(Note 7)	ST/Tm.
SOLANALES.					
CONVOLVULACEÆ (74–251).					
Convolvulus sepium Linn.	Bb†	Pink	Cyan.	Dimon. (11)	ST/Tm.
C. sepium Linn. var. *Soldanella*	A	Red/Blue	Cyan.	Mon.	ST/Tm.
Ipomœa congesta R.Br.	Ba	Red/Blue	Peon.	Bios. ?	NG.
I. Pes-capræ Roth. (Note 5)	A	Red/Blue	Cyan.	Mon.	Tr.
I. Quamoclit Linn. ..	A	Red	Cyan.	PG.	NG.
I. sp.	A	Red/Blue	Cyan.	Bios.	NG.
Polymeria calycina R.Br.	A	Pink	Malv.	Mixture	ST.

Table 1.—*Continued.*

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—*Cont.*					
SOLANALES.—*Continued.*					
Solanaceæ (74–250).					
Solanum aviculare Forst.	A	Blue	Nitrogenous ?	(Note 8)	ST/Tm.
S. campanulatum R.Br.	A	Blue	Pet.+Malv.	Dimon.	ST.
S. nigrum Linn.	Fruit	Blue/Black	Malv. X	Mixture	G.
S. stelligerum Sm.	A	Blue	Pet.+Malv.	Dimon.	Tr/ST.
S. vescum F. Muell.	A	Blue	Malv.	Dimon.	ST/Tm.
Do.	Fruit	Blue	Malv.	Mixture	
CAMPANALES.					
Stylidaceæ (71–246).					
Stylidium gramnifolium Swartz.	A†	Pink	Cyan.	Mon.	ST/Tm.
S. lineare Swartz.	A	Pink	Cyan.	Mon.	ST.
Goodeniaceæ (71–245).					
Dampiera Brownii F. Muell.	A	Blue	Delph.	Mixture	ST/Tm.
D. stricta R.Br.	A	Blue	Malv.	Mixture	ST/Tm.
Goodenia (*paniculata* Sm. ?)	Bc	Red	Malv.	Mixture	G.
Scævola hispida Cav.	A	Blue	Delph.	Mixture	ST/Tm.
S. (*Hookeri* F. Muell. ?)	Ba	Red	Malv.	Bios.	Tm.
S. microcarpa Cav.	A	Blue	Delph.	Dimon.	ST/Tm.
S. suaveolens R.Br.	A	Blue	Delph.	Dimon.	G.
Do.	Fruit	Blue	Delph.	PG.	
Lobeliaceæ (71–244).					
Isotoma axillaris Lindl.	A	Blue	Malv. X	Mixture	ST/Tm.
Lobelia anceps Thunb.	Bb	Blue	Malv. (Fe+)	PG.	ST/Tm.
L. dentata Cav.	A	Blue	Delph.	Bios.	ST.
L. purpurascens R.Br.	A	Blue	Malv. (Fe+)	Mixture	ST/Tm.
Campanulaceæ (71–243).					
Wahlenbergia gracilis DC.	A†	Blue	Delph.	Dimon.	G.
ASTERALES.					
Compositæ (67–238).					
Brachycome decipiens J. Hook. or *B. scapiformis* DC.	Bc	Red/Blue	Delph.	Dimon.	ST/Tm.
Erecthites valerianifolia DC.	A	Red/Blue	Cyan.	Digly.	NG.
Helipterum Manglesii F. Muell.	Bracts	Pink	Peon. (11)	Bios.	WA.
Humea elegans Sm.	A	Red/Blue	Peon.	Indef. (10)	Tm.
Olearia dentata Moench.	Bb	Blue	Malv.	Bios.	Tm.
Vernonia cinerea Less.	A†	Red/Blue	Malv. X	Digly.	G.
RUBIALES.					
Rubiaceæ (66–232).					
Opercularia aspera Gaertn.	Bc	Red/Blue	Abnormal (9)		ST/Tm.
Pomax umbellata Sol.	Bc	Red	Delph.	PG.	G.
APOCYNALES.					
Apocynaceæ (65–230)					
Ochrosia elliptica Labill.	Fruit	Red	Cyan.	Bios.	Tr.
LOGANIALES.					
Oleaceæ (64–229).					
Olea paniculata R.Br.	Fruit*	Blue/Black	Cyan.	Mon.	Tr/ST.
EBENALES.					
Sapotaceæ (61–222).					
Sideroxylon australis Benth.	Fruit	Blue/Black	Cyan.	PG.	Tr/ST.

TABLE 1.—*Continued.*

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—*Cont.*					
ERICALES.					
EPACRIDACEÆ (60–217).					
Astroloma humifusum R.Br.	A	Red	Cyan.	Mon.	Tm.
Dracophyllum secundum R.Br.	Ba	Red	Cyan.	PG.	33/36
Epacris longiflora Cav. ..	Ba†	Red	Cyan.	Mon.	Tm.
E. longiflora var. *superba* (3)	*	Red	Cyan.	Mon.	
E. microphylla R.Br. ..	Bracts	Red	Cyan.	PG.	ST/Tm.
E. obtusifolia Sm. (6) ..	B†*	Red	Cyan.	Mon.	ST/Tm.
E. pulchella Cav. ..	Bb	Red	Cyan.	Mon.	ST.
E. reclinata Cunn. ..	Ba†	Red	Cyan.	Mon.	33/36
Leucopogon amplexicaulis R.Br.	B	Red	Cyan.	Mon.	33/36
L. pulchellus Sond. ..	Bc	Red	Cyan.	Mon.	WA.
Lissanthe sapida R.Br.	Fruit	Red	Cyan.	Mon.	33/36
L. strigosa R.Br. ..	B†	Red	Cyan.	PG.	ST/Tm.
Styphelia tubiflora Sm. ..	A	Red	Malv. X	A-sugar	33/36
Trochocarpa laurina R.Br.	Fruit	Blue/Black	Cyan.	Mixture	Tr/ST.
Woollsia pungens F. Muell.	Bb†	Pink	Malv.	Mon.	ST.
UMBELLIFLORÆ.					
UMBELLIFERÆ (59–213).					
Actinotus helianthi Labill.	Bc	Red	Cyan. + Peon.	PG.	ST.
ARALIACEÆ (59–212).					
Panax sambucifolius Sieb.	Fruit	Blue	Malv.	Digly.	ST/Tm.
SAPINDALES.					
SAPINDACEÆ (57–198).					
Dodonæa viscosa Linn. var. *purpurea*	A*	Red	Cyan.	Mon.	
Do.	Fruit*	Red/Blue	Cyan.	Mon.	
Nephelium leiocarpum F. Muell..	Fruit	Red	Peon.	PG.	ST/Tm.
MELIALES.					
MELIACEÆ (56–197).					
Melia azedarach Linn. var. *australasica* DC. ..	A*	Red/Blue	Cyan.	Mon.	Tr/ST.
RUTALES.					
RUTACEÆ (55–194).					
Boronia Bakeriana F. Muell.	A†	Pink	Malv.	Dimon.	33/36
B. elatior Bartl. (3) ..	A*	Pink	Malv. (Trace Fe+)	Dimon.	WA.
B. heterophylla F. Muell.		Red	Malv.	Bios.	WA.
B. ledifolia Gay.	A	Pink	Malv.	Mon.	ST.
B. ledifolia var. *triphylla* ..	A	Pink	Malv.	Dimon.	33/36
B. megastima Nees ..	Bb*	Red	Delph. X (11)	Bios.	WA.
B. microphylla Sieb. ..	A	Pink	Malv. (some Fe+)	Dimon.	ST.
B. pinnata Sm.	A	Pink	Malv.	Dimon.	ST/Tm.
B. polygalifolia Sm. ..	A†	Pink	Malv.	PG.	ST/Tm.
B. serrulata Sm.	A†	Pink	Malv.	Dimon.	33/36
Citrus australasica F. Muell.	A†*		Malv.	Mon.	ST.
Correa speciosa Andr. ..	Ba†	Red.	Cyan.	PG.	ST/Tm.
Correa speciosa var. *ventricosa* (1)	*	Red	Cyan.	PG.	

TABLE 1.—*Continued.*

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—*Cont.*					
RUTALES.—*Continued.*					
RUTACEÆ.—*Continued.*					
Eriostemon Crowei F. Muell.	A	Pink	Malv.	Mon.	ST/Tm.
E. lanceolatus Gaertn.	A	Pink	Malv.	PG.	ST/Tm.
E. hispidulus Sieb.	A†	Pink	Cyan. (+Peon. ?)	Digly.	ST.
Philotheca australis Rudge	A	Red/Blue	Delph.	A-sugar	ST.
RHAMNALES.					
AMPELIDACEÆ (54–193).					
Vitis hypoglauca F. Muell. (4)	Fruit	Blue-Black	Malv.	Mon.	G.
CELASTRALES.					
STACKHOUSIACEÆ (51–181).					
Stackhousia linarifolia Cunn.	Bc		Malv. (Fe+)	Dimon.	ST/Tm.
URTICALES.					
MORACEÆ (50–167).					
Ficus Bellingeri C. Moore	Fruit*	Red	Cyan.	Mon.	ST.
F. macrophylla Desf.	Fruit*	Red	Malv.	PG.	ST.
F. rubiginosa Desf.	Fruit*	Red	Malv.	Mixture	ST.
F. sp.	Fruit	Red	Cyan.	Mon. or PG.	NG.
F. sp.	Fruit	Red	Cyan.	PG.	NG.
F. sp.	Fruit	Red	Cyan.	PG.	NG.
CASUARINALES.					
CASUARINACEÆ (49–164)					
Casuarina Cunninghamiana Miq.	A	Red	Malv. (Fe+)	Mon.	G.
C. distyla Vent.	A ♂	Red	Delph.	A-sugar	ST/Tm.
Do.	A ♀	Red	Delph.	A-sugar	
C. glauca Sieb.	A* ♂	Red	Cyan.	Mon.	ST/Tm.
Do.	A ♀	Red	Delph. +Cyan.	Mon.	
C. nana Sieb.	A ♂	Red	Cyan.	Mon.	Tm.
Do.	A ♀	Red	Delph. +Cyan.	Mon.	
C. paludosa Sieb.	A	Red	Cyan.	PG.	Tm.
C. rigida Miq.	A ♂	Red	Cyan.		ST/Tm.
Do.	A ♀	Red	Delph. +Cyan.	Mon.	
C. suberosa Ott. et Dietr.	A ♂	Red	Peon. +Cyan.	Mon.	G.
Do.	A ♀	Red	Cyan.	PG.	
LEGUMINOSÆ.					
PAPILIONACEÆ (41–148).					
Aotus villosa Sm.	Bb	Red/Blue	Malv.	PG.	ST/Tm.
Bossiœa cinerea R.Br.	Bb	Red	Cyan.	Dimon. (10)	Tm.
B. ensata Sieb.	Bb	Red	Malv.	Mon.	ST/Tm.
B. heterophylla Vent.	Bb	Red	Delph. (X ?)	Mixture	ST/Tm.
B. microphylla Sm.	Bb	Red	Malv.	Mon.	ST/Tm.
B. prostrata R.Br.	Bc	Red	Peon.	Mon.	ST/Tm.
B. rhombifolia Sieb.	Fruit	Red	Cyan.	Mon.	ST.
Brachysema lanceolata Meissn.	A*	Red	Cyan.	Mon. (10)	WA.
Canvalia obtusifolia DC.	A	Red/Blue	Malv.	PG. or Mon.	NG.
Castanospermum australe Cunn. et Fras.	Bb*	Red	Cyan.	Mon.	Tr.

TABLE 1.—*Continued.*

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—*Cont.*					
LEGUMINOSÆ.—*Continued.*					
Papilionaceæ.—*Continued.*					
Chorizema cordatum Lindl.	Ba*	Pink	Malv.	Mon.	WA.
Clianthus Dampieri Cunn. (11)	A	Red	Pel.+Cyan.	Mon.	ST.
Clitoria ternatea Linn. ..	A	Blue	Delph.	Dimon.	NG.
Daviesa corymbosa Sm. ..	Bb	Red	Cyan.	Bios.	ST/Tm.
D. ulicina Sm.	Bb	Red	Delph. X	Mon.	ST/Tm.
Desmodium latifolium DC.	A	Blue	Malv.	Mon.	NG.
D. polycarpum DC ..	A	Red/Blue	Malv.	PG.+Digly.	NG.
Dillwynia cinerascens R.Br.	Bb	Red	Malv.	PG. ?	Tm.
D. ericifolia Sm. ..	Fruit	Red	Cyan.	PG.	ST/Tm.
D. floribunda Sm. ..	B	Red	Malv.	Dimon.	ST/Tm.
D. juniperina Sieb. ..	B	Red	Malv.	PG.	ST/Tm.
Erythrina indica Lam. ..	A*	Red	Pel.	Bios.	Tr.
Glycine clandestina Wendl.	A	Blue	Malv. (11)	Dimon.	G.
Hovea heterophylla Cunn...	A	Red/Blue	Cyan. ?	Mixture	ST/Tm.
H. linearis R.Br. ..	A	Red/Blue	Malv.	PG.	ST.
H. longifolia R.Br. ..	A	Red/Blue	Malv.	PG.	G.
H. pungens Benth. ..	A	Red/Blue	Malv. +Cyan.	Dimon.	WA.
H. (*trisperma* Benth. ?) ..	A	Red/Blue	Malv.	Dimon.	WA
Indigofera australis Willd.	A	Red/Blue	Malv.	(11)	ST/Tm.
Isotropis cuneifolia Sm. ..	B	Red	Cyan.	Mon.	WA.
Jacksonia scoparia R.Br.	B	Red/Blue	Malv.	Mon.	ST.
Kennedya coccinea Vent.	A*	Red	Peon.	Mon.	WA.
K. Comptoniana Benth. ..	A*	Red/Blue	Malv.	Dimon.	WA.
K. monophylla Vent. ..	A	Red/Blue	Malv. (11)	Dimon.	ST/Tm.
K. monophylla var. ..	A*	Red/Blue	Malv.	Dimon.	
K. nigricans Lindl. ..	A*	Red/Blue	Pet.	Dimon.	WA.
K. prostrata R.Br. ..	A	Red	Cyan.	Bios.+Mon.	ST/Tm.
K. rubicunda Vent. ..	A	Red	Peon. (11)	Mon.	G.
Maniltoa grandiflora Scheff.	Bracts	Pink	Cyan.	Mon.	NG.
Mirbelia grandiflora Ait.	Bb	Red	Malv.	Mon.-A	33/36
M. reticulata Sm. ..	A	Red/Blue	Malv.	Mon.	ST.
Oxylobium callistachys Benth.	Bb*	Red/Blue	Malv.	Mon. or PG.	WA.
O. trilobatum Benth. ..	Bb	Red/Blue	Malv.	Mon.	ST/Tm.
Phyllota phylicoides Benth.	Bc	Red	Malv.	PG.	ST.
Platylobium formosum Sm.	Bb	Red	Malv.	Mon.	ST/Tm.
P. obtusangulum Hk. ..			Malv.	Mon.	Tm.
Pultenœa daphnoides Wendl.	Bb	Red	Malv.	Mon.-A	Tm.
P. incurvata Cunn. ..	Bb	Red	Malv.	Mon.	33/36
P. microphylla Sieb. ..	B	Red	Pet.	PG.	ST.
P. retusa Sm.	B	Red	Malv. (some Fe+)	PG.	ST/Tm.
P. scrabra R.Br.	Fruit		Cyan.	Mon.	Tm.
P. sp.	B		Cyan.	PG.	
Sphœrolobium vimineum Sm.	B	Red	Malv.	PG.	Tm.
Swainsona coronillæfolia Salisb.	A†*	Red/Blue	Delph. X (11)	Dimon.	ST.
Templetonia retusa R.Br.	A*	Red	Malv. (+cyan. ?)	Mon.	WA.
Viminaria denudata Sm. ..	B	Red	Cyan.	Mon.	ST/Tm.
Mimosaceæ (41–147).					
Acacia Baileyana F. Muell.	Fruit*	Red	Cyan.	Mon.	ST/Tm.
A. decurrens Willd. var. *normalis*	Fruit	Red	Delph. X	Mon. or PG.	ST/Tm.

TABLE 1.—*Continued.*

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—*Cont.*					
LEGUMINOSÆ.—*Continued.*					
MIMOSACEÆ.—*Continued.*					
A. juniperina Willd. ..	Fruit	Red	Malv.	PG.	ST/Tm.
A. myrtifolia Willd. ..	Bc	Red	Cyan. +Peon.	Mon.	ST/Tm.
A. suaveolens Willd. ..	Fruit	Red	Delph.	Mon.	ST/Tm.
ROSALES.					
ROSACEÆ (40–143).					
Acæna sanguisorbe Vahl.	Ba	Red	Cyan.	Mon.	ST/Tm.
Rubus parvifolius Linn. ..	Fruit	Red	Cyan.	PG.	ST/Tm.
R. rosifolius Sm.	Fruit	Red	Peon.	Mon.	G.
R. sp.	Fruit	Red	Pel.	PG.	NG.
CUNONIALES.					
CUNONIACEÆ (39–137).					
Ceratopetalum apetalum D. Don.	A†	Red	Cyan.	PG.	33/36
C. gummiferum Sm. ..	A	Red	Cyan.	Mon.	33/36
EUPHORBIALES.					
EUPHORBIACEÆ (38–136).					
Breynia cernua F. Muell.	Fruit	Red	Peon. + some Cyan.	PG.	NG.
B. oblongifolia F. Muell. ..	Fruit	Red	Cyan.	Bios. ?	Tr/ST.
Micrantheum ericoides Desf.	Bb	Red	Delph.	PG.	ST.
Do.	Fruit	Red	Delph.	Mon.	
Phyllanthus thymoides Sieb.	Fruit	Red	Delph.	PG.	ST/Tm.
Ricinocarpus pinifolius Desf.	Bc	Red	Delph.	PG.	ST/Tm.
MALVALES.					
MALVACEÆ (36–132).					
Lagunaria Patersoni Ait.	*	Pink	Malv.	Dimon.	Tr.
TILIALES.					
STERCULIACEÆ (35–130).					
Abroma fastuosa R.Br. ..	Bb	Red/Blue	Cyan.	Mon.	NG.
Kleinhovia hospita Linn.	A	Pink	Cyan.	Mon.	NG.
Sterculia acerifolia Cunn...	A*	Red	Peon.	Mon.	ST.
S. discolor F. Muell. ..	A*	Pink	Cyan.	Indef. (10)	ST.
S. quadrifida R.Br. ..	B*	Red	Cyan. +Peon.	Mon.	Tr/ST.
TILIACEÆ (35–128).					
Elæocarpus obovatus G. Don. (2)	*		Cyan.	PG.	ST.
E. reticulatus Sm. ..	A†	Pink	Malv.	Mon.	ST/Tm.
Do.	Fruit	Blue	Malv.	Mon.	
MYRTALES.					
MELASTOMACEÆ (33–120).					
Melastoma malabathricum Linn.	A†*	Blue	Indef. (12)	Digly.	Tr/ST.
LECYTHIDACEÆ (33–119).					
Barringtonia (*calyptrocalyx* K. Schum. ?)	A	Red	Malv. (some Fe+)	PG.	NG.
MYRTACEÆ (33–118).					
Angophora cordifolia Cav.	(13)	Red	Cyan.	PG.	33/36
A. intermedia DC. ..	(13)	Red	Delph.	PG.	ST/Tm.
A. lanceolata Cav. ..	(13)	Red	Delph.	PG.	ST/Tm.

TABLE 1.—*Continued.*

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—*Cont.*					
MYRTALES.—*Continued.*					
MYRTACEÆ.—*Continued.*					
Callistemon acuminatus Cheel	*	Red	Pet.	Mon.	
C. citrinus Stapf. var. *splendens*	A*	Red	Cyan. (2)	Digly.	
C. hortensis Hort.	*	Red	Delph.	PG.	
C. lanceolatus DC.	A	Red	Cyan.	Mon.	G.
C. lilacina Cheel	A*	Red/Blue	Indef. (12)		
C. lilacina var. *carmina*	A*	Red	Pet.	Mon.	
C. pinifolius DC.	Bc	Red	Cyan.	Mon.	33/36
C. speciosus DC. (3)	A*	Red	Cyan. + Delph.	Dimon.	WA.
C. viminalis (Sol.) Cheel	A*	Red	Pet.	Mon.	ST.
Calothamnus chrysantherus F. Muell.	A*	Red	Malv.	Bios.	WA.
C. quadrifidus R.Br.	A*	Red	Indef. (12)	Indef. (10)	WA.
C. sanguineus Labill.	A*	Red	Cyan. (some Fe −)	Mon.	WA.
C. villosus R.Br.	A*	Red	Malv.	Mon.	WA.
Chamælaucium uncinatum Schau.	A†*	Pink	Malv. (some Fe +)	Dimon.	WA.
Darwinia fascicularis Rudge	Bracts	Red	Cyan.	Mon.	ST.
Eucalyptus ficifolia F. Muell.	A*	Red	Peon. ? (14)	Bios.	WA.
Eugenia Smithii Poir.	Fruit	Red/Blue	Malv.	Bios.	G.
Kunzea capitata Reichb.	A	Red/Blue	Malv.	Bios.	ST/Tm.
Leptospermum citratum Cheel, Challinor et Penfold	Bc*	Pink	Malv.	Mon.	
L. lævigatum F. Muell.	A	Pink	Delph.	Mon.	ST/Tm.
L. scoparium Forst.	A†*	Pink	Malv. (some Fe +)	PG.	ST/Tm.
L. scoparium var. *Nicollsii* (6)	A*	Red	Cyan.	Mon.	
L. scoparium var. *persiciflorum*	A	Pink	Malv.	PG.	
Melaleuca crassifolia Benth.	A*	Pink	Malv. ?	Mon. or PG.	WA.
M. elliptica Labill.	A*	Red	Malv. (+cyan. ?)	PG.	WA.
M. ericifolia Sm.	A†	Red	Delph.	PG. ?	ST/Tm.
M. hypericifolia Sm.	A*	Red	Delph.	A-sugar	ST/Tm.
THEALES.					
SAURALACEÆ (32–113).					
Saurauia sp.	Fruit	Red	Cyan.	Mixture	NG.
PASSIFLORES.					
PASSIFLORACEÆ (29–101).					
Passiflora fœtida Linn.	Bb	Red/Blue	Malv.	Mon.	NG.
Do.	Bracts	Red	Delph.	PG.	
P. Herbertiana Lindl.	Bb†	Red	Peon.	PG.	G.
PITTOSPORALES.					
TREMANDRACEÆ (26–90).					
Tetratheca ciliata Lindl.			Indef. (12)		Tm.
T. ericifolia Sm.	A	Red/Blue	Malv. ? (Fe +)	Mixture	Tm.
T. thymifolia Sm.	A	Red/Blue	Malv.	Mixture.	ST/Tm.

Table 1.—*Continued.*

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—*Cont.*					
DILLENIALES.					
Dilleniaceæ (24–85).					
Hibbertia Billardieri F.Muell.	Calyces		Delph.	PG.	ST/Tm.
H. volubilis Andr. (2) ..	Calyces*	Red	Cyan.	Mon.	Tr/ST.
PROTEALES.					
Protaceæ (23–84).					
Banksia ericifolia Linn. ..	Fruit	Red	Delph.	Mon.	ST.
Conospermum ericifolium Sm.	A	Red/Blue	Cyan.	Bios.	33/36
C. longifolium Sm. ..	A†	Red/Blue	Pet.	PG.	33/36
C. tenuifolium R.Br. ..	A†	Red/Blue	Delph.	Dimon. +Mon.	33/36
C. sp.	A	Blue	Pet.	PG.	WA.
Grevillea acanthifolia Cunn.	A	Red/Blue	Delph.	Bios.	33/36
G. Banksii R.Br. ..	A†*	Red	Cyan.	PG.	ST.
G. bipinnatifida R.Br. ..	A	Red	Cyan.	PG. or Mon.	WA.
G. buxifolia R.Br. ..	Bb	Red	Cyan.	Bios.	33/36
G. Caleyi R.Br.	A*	Red	Cyan.	Bios.	33/36
G. juniperina R.Br. ..	Bb†	Pink	Malv.	PG.	33/36
G. lanigera Cunn. ..	Bc	Red	Delph.		Tm.
G. laurifolia Sieb. ..	A	Red	Delph.	PG.	33/36
G. linearis R.Br. ..	A	Red	Cyan.	PG.	33/36
G. punicea R.Br.	A	Red	Cyan. (11)	Mon.	33/36
G. robusta Cunn.	Bb*	Red	Delph.	PG.	ST.
G. sericea R.Br.	A	Pink.	Malv.	Dimon.	33/36
G. sphacelata R.Br. ..	Bc	Red	Cyan.	PG.	ST/Tm.
G. trinervis R.Br. ..	A	Pink	Cyan.	Mixture	ST.
Hakea laurina R.Br. ..	B*	Pink	Cyan.	Mixture	WA.
H. propinqua Cunn. ..	Fruit		Delph.		33/36
H. saligna Knight ..	Fruit		Delph.	Mixture	ST.
Lambertia formosa Sm. ..	A	Red	Malv.	Mon.	33/36
Persoonia linearis Andr.	Fruit	Blue/Black	Malv.	PG.	ST/Tm.
P. pinifolia R.Br. ..	Fruit	Blue/Black	Cyan.	PG.	33/36
P. myrtilloides Sieb. ..	Fruit	Blue/Black	Delph.	PG.	Tm.
Telopea speciosissima R.Br.	A	Red	Cyan.	Mon.	33/36
THYMELÆALES.					
Thymeleaceæ (22–181).					
Phaleria Neumanni F. Muell.	Bc*		Delph. ?	Mon.	Tr.
Do.	Fruit*	Red	Delph.	Mon.	
Pimelia linifolia Sm. ..	Bc†	Pink	Delph.	Digly.	G.
LYTHRALES.					
Halorrhagaceæ (21–78).					
Halorrhagis teurcroides Gray	Bb	Red	Delph.	Mon.	ST/Tm.
Sonneratiaceæ (21–74).					
Sonneratia alba Sm. ..	A†	Red	Cyan.	Bios. + PG. ?	NG.
GERANIALES.					
Geraniaceæ (20–67).					
Pelargonium australe Willd.	A	Pink	Delph.	Dimon.	G.
Linaceæ (20–65).					
Linum marginale Cunn. ..	A	Red/Blue	Delph.	Dimon.	G.
CHENOPODIALES.					
Chenopodiaceæ (19–61).					
Atriplex cinerea Poir. ..	A♂	Red	Nitrogenous		ST/Tm.
Suæda maritima Dumont (3)	A†*	Red	Nitrogenous		G.

TABLE 1.—*Continued.*

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—*Cont.*					
POLYGONALES.					
POLYGONEACEÆ (18–57).					
Polygonum sp.			Cyan.	PG.	
CARYOPHYLLALES.					
PORTULACACEÆ (17–56).					
Portulaca oleracea Linn. (5)	Stems	Red	Nitrogenous		G.
FICOIDACEÆ (17–55).					
Mesembryanthemum æquilaterale Haw.	A	Red/Blue	Nitrogenous +small amount of cyan.		G.
Sesuvium portulacastrum Linn. (5)	Bb	Pink	Nitrogenous		ST.
SARRACENIALES.					
DROSERACEÆ (15–48).					
Drosera auriculata Backh.	(15)	Red	Cyan.	Mixture	ST/Tm.
D. binata Labill.	(15)	Red	(Malv. +Cyan. ?)	Mixt.-A	ST/Tm.
D. pygmœa DC.	(15)	Red	Pel.	A-sugar	ST/Tm.
D. spathulata Labill. ..	(15)	Red	Pel.		G.
SAXIFRAGALES.					
SAXIFRAGACEÆ (14–47).					
Bauera rubioides Andr. ..	A†	Pink	Indef. (12)	PG.	ST/Tm.
POLYGALES.					
POLYGALEACEÆ (13–42).					
Bredemeyera volubile Steetz		Red/Blue	Delph.	Bios.	ST/Tm.
Comesperma ericinum DC.	A	Red/Blue	Cyan.	Bios.	ST/Tm.
Polygala paniculata Linn. var. *canchalagna* ..	Bracts	Blue	Cyan.	Dimon.	NG.
VIOLALES.					
VIOLACEÆ (12–40).					
Hybanthus filiformis F. Muell..	A	Blue	Delph.	Dimon.	ST/Tm.
Viola betonicifolia Sm. ..	A	Red/Blue	Malv. X	Dimon.	ST/Tm.
V. hederacea Labill. ..	A†	Red/Blue	Delph.	Dimon.	ST/Tm.
V. hederacea var. ..	A	Red/Blue	Delph.	Dimon.	
LAURALES.					
LAURACEÆ (3–11).					
Cryptocarya glaucescens R.Br.	Fruit	Blue/Black	Cyan.	Mixture	Tr/ST.
MONIMIACEÆ (3–10).					
Doryphora Sassafras Endl. (2)	†*		Cyan.	PG.	ST.
MAGNOLIALES.					
WINTERACEÆ (1–2).					
Drimys dipetala F. Muell.. .	Fruit	Red	Cyan.	Mixture	ST.
MONOCOTYLEDONS.					
GRAMINALES.					
GRAMINEÆ (105–332).					
Brachiaria reptans Gard. et C.E.H.	Fruit	Red	Cyan.	Mon.	NG.
Pennisetum macrostachyum Trin.	Bc	Red	Malv.	Mon.	NG.

Table 1.—*Continued.*

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
MONOCOTYLEDONS.—*Continued.*					
GRAMINALES.—*Continued.*					
Gramineæ.—*Continued.*					
Saccharum spontaneum Linn.	Fruit	Red	Cyan.	Mon.	NG.
Spinifex hirsutus Labill. ..	Bracts	Red	Malv.	PG. or Mon.	G.
Themeda Forskalii Hack.		Red	Delph. ?	PG.	
JUNCALES.					
Restionaceæ (103–330).					
Leptocarpus tenax R.Br. ..	Bracts	Red	Malv.	Mon. or PG.	Tm.
ORCHIDALES.					
Orchidaceæ (103–236).					
Acianthus fornicatus R.Br.	Bb	Red/Blue	Cyan.	Bios.	ST.
Caladenia carnea R.Br. ..	Ba†	Pink	Cyan. + some Malv.	Bios.	ST/Tm.
C. Patersoni R.Br. ..	Bb	Red/Blue	Malv. (trace Fe+)	Bios.	ST/Tm.
Caleana major R.Br. ..	A	Red	Cyan.	A-sugar	ST/Tm.
Dipodium punctatum R.Br.	A	Red/Blue	Cyan.	A-sugar	G.
Diuris aurea Sm. ..	Bb	Red	Cyan.	Dimon.	ST.
D. elongata Swartz. ..	A	Red/Blue	Malv.	Bios.	ST/Tm.
D. sulphurea R.Br. ..	Bb	Red/Blue	Malv. (Fe+)	Dimon.	ST/Tm.
Glossodia major R.Br. ..	A†	Red/Blue	Delph.	Dimon. (11)	ST/Tm.
G. minor R.Br.	A†	Blue	Pet.	Dimon.	ST/Tm.
Prasophyllum (*elatum* R.Br. ?)	Ba	Red/Blue	Cyan.	Dimon.	Tm.
Thelymitra ixoides Swartz ..	A	Blue	Cyan.	Dimon.	ST/Tm.
T. venosa R.Br.	A	Blue	Cyan.	Mon.	Tm.
HÆMODORALES.					
Hæmodoraceæ (100–317).					
Anigozanthos flavida Red.	Bb†*	Red	Cyan.	PG.	WA.
A. Manglesii D. Don. ..	Bb†	Red	Cyan.	Indef. (10)	WA.
PALMALES.					
Palmæ (97–314).					
Livistona australis Mart. ..	Fruit	Blue/Black	Cyan.	Mon. + Digly.	ST.
AGAVALES.					
Agavaceæ (96–313).					
Cordyline stricta Endl. ..	A*	Red/Blue	Malv. (Fe+)	PG. + Digly.	ST.
C. sp.	Fruit	Red	Pel.	PG.	NG.
Doryanthes excelsa Corr. ..	A	Red	Cyan.	Mon.	ST.
D. Larkini C. Moore ..	A*	Red	Cyan.	Mixture	ST.
D. Palmeri Hill	A*	Red	Cyan.	(11)	ST.
Do.	Fruit*	Red	Cyan.	PG.	
Xanthorrhœaceæ (96–312).					
Xerotes longifolia R.Br. ..	Fruit		Malv.	PG.	G.
IRIDALES.					
Iridaceæ (94–307).					
Patersonia glabrata R.Br.	A	Blue	Malv.	Dimon.	ST/Tm.
P. glauca R.Br.	A	Blue	Malv.	Dimon.	ST/Tm.
P. sericia R.Br.	A	Blue	Malv.	Dimon.	ST/Tm.
ARALES.					
Araceæ (91–302).					
Alocasia sp.	A	Red	Cyan. + Delph.	PG.	NG.
Gymnostachys anceps R.Br.	Fruit	Blue/Black	Cyan.	Mixture	Tr/ST.

TABLE 1.—*Continued.*

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
MONOCOTYLEDONS.—*Continued.*					
ALSTRŒMERIALES.					
Philesiaceæ (90–301).					
Eustrephus Brownii F. Muell.	A	Red/Blue	Malv.	Bios.	G.
LILIALES.					
Smilaceæ (89–297).					
Smilax glycyphylla Sm. ..	Fruit	Blue/Black	Cyan.	Mon.	Tr/ST.
S. (*timorensis* DC. ?) (16)	Fruit	Red	Peon.	Bios.	NG.
Do.	Fruit	Blue	Cyan.	Bios.	
Liliaceæ (89–293).					
Arthropodium sp.	A	Red/Blue	Cyan.	PG.	
Blandfordia flammea Hook.	Ba	Red	Cyan.	Bios.	ST.
B. grandiflora R.Br. ..	Ba*	Red	Cyan.	Bios. +Mon.	ST.
B. nobilis Sm.	Ba	Red	Cyan.	Bios.	33/36
Burchardia umbellata R.Br.	Bb	Red	Cyan.	Bios.	ST/Tm.
Cæsia vittata R.Br. ..	Bb†	Blue	Delph.	Bios.	ST/Tm.
Dianella cærulea Sims ..	A	Blue	Delph.	Bios.	Tr/ST.
Do.	Fruit	Blue	Delph.	Bios.	
D. sp.	Fruit	Blue	Delph.	Bios.	
Sowerbœa juncea Sm. ..	A	Red/Blue	Delph.	Dimon.	ST/Tm.
Stypandra glauca R.Br. ..	A	Blue	Delph.	Bios.	ST/Tm.
S. sp.	A	Blue	Delph.	Bios.	
Thysanotus junceus R.Br.	A	Red/Blue	Delph.	Bios.	ST.
Wurmbea dioica F. Muell.	Bb†	Red/Blue	Cyan. +Peon.	Dimon.	ST/Tm.
ZINGIBERALES.					
Zingiberaceæ (88–290).					
Costus (*speciosus* Sm. ?) ..	A	Red	Cyan.	Mon.	NG.
Curcuma longa Linn. ..	A	Red	Cyan.	PG.	NG.
Musaceæ (88–287).					
Musa sp.	Bracts	Red	Cyan. +Malv.	Mon.	NG.
COMMELINALES.					
Commelinaceæ (84–280).					
Commelina cyanea R.Br.	A	Blue	Delph.	PG.	Tr/ST.
JUNCAGINALES.					
Juncaginaceæ (80–271).					
Triglochin procera R.Br.	Bc		Malv. (Fe+)	Dimon.	G.

Notes to Table 1.

The figures quoted alongside the names of the families are those allotted by Hutchinson in his classification. The first figure indicates the order, and the second the family.

(i) *Mode of Occurrence.*

* Collected from cultivated plants.

† The anthocyanin is often absent from the flowers. (It is well known that practically all species which have flowers coloured by anthocyanins occasionally appear with the anthocyanin absent.) A separate analysis indicates that the distribution of anthocyanins is much the same in these species as in normal species.

A Flowers completely or mostly coloured by anthocyanin. Other pigments, if present, completely or largely masked by the anthocyanin.

B Flowers coloured by anthocyanin together with large amounts of other pigments (carotenoids, yellow and white anthoxanthins, chlorophyll, etc.).

Ba—Anthocyanin colouring most of the flower.
Bb—Anthocyanin colouring only a small amount of the flower (often as spots or streaks on the petals).
Bc—Anthocyanin in very small amount (often colouring a minor part of the flower).

(ii) *Colour of Anthocyanin.* (Not necessarily always the colour of the whole flower.)

Red	Includes all shades of red—orange red, scarlet, crimson, etc.—excluding pink and shades with a bluish tinge.
Red/Blue	Ranges from red with a bluish tinge to blue with a reddish tinge. Includes mauve, lilac, violet, etc. Also includes flowers with separate areas of red and blue. Generally well on the blue side.
Blue	No reddish tinge.

(iii) *Anthocyanidin.*

Malv. X	Malvidin+delphinidin and/or petunidin.
Delph. X	Delphinidin+malvidin (+petunidin ?).
Malv. Fe +	Malvidin giving positive ferric test due to admixture with delphinidin (and/or petunidin) or cyanidin.

(iv) *Glycoside Type.* The nomenclature is that used in previous surveys except that the enumeration is omitted, it being understood that the sugars are attached in the usual positions.

Mixt.	Mixture of diglycoside and monoglycoside.
Digly.	Dimonoside or bioside.
A	Acylated.
A-sugar	The sugar is attached to an acyl group which is attached to the anthocyanidin.

(v) *Distribution.*

NG.	Species collected in New Guinea (Huon Gulf district. Latitude 7° S.). Many of these extend into north Queensland.
WA.	Species native to Western Australia and not occurring in eastern Australia. Almost all the species listed are restricted to the south-western corner. (Latitude from approx. 28° S. to 35° S.). The remainder of the species examined are from eastern Australia and are almost all native to the coastal and dividing range section though many extend inland as well. For the purpose of analysis of the results they have been divided into the following geographical subdivisions based on the distributions given for each species in the Floras of the various States.
Tr.	Tropical. Species growing mainly or entirely in central and north Queensland (down to Lat. 24° S.).
ST.	Sub-tropical. Species growing in south Queensland and northern N.S.W. Approximately between latitudes 24° S. and 32° S.
33°/36°	Species whose habitat appears to be restricted to this range of latitude. (The comparatively large number of such species is due to the fact that a large number of the plants examined were collected in this area.)
ST/Tm.	Sub-tropical to temperate. Species whose habitat extends from south Queensland into Victoria or Tasmania. (South of Lat. 26° S.)
Tm.	Temperate. Species extending from southern N.S.W. into Victoria and Tasmania (South of Lat. 36° S.)
G.	General distribution. Species extending from north or central Queensland into Victoria and Tasmania and westwards. (Victorian species were collected while one of us (D.E.W.) was at the Chemistry Department of the University of Melbourne.)

Miscellaneous.

1 Lawrence *et al.*, 1938.
2 Price and Sturgess, 1938.
3 Lawrence *et al.*, 1939.
4 Cornforth, 1939.
5 Taylor, 1940.
6 Beale *et al.*, 1941.
7 The material was very readily extracted by 1% hydrochloric acid yielding a solution of the normal red colour which turned black in 24 hours.

8 The extract gave the tests for a bioside but the pigment was destroyed by acid hydrolysis.

9 The dark red extract gave the distributions of a pentoseglycoside but was not hydrolysed by boiling with 15% hydrochloric acid for 15 minutes. Apparently a non-anthocyanin water-soluble pigment.

10 The extract contained a pigment with a much higher distribution to amyl alcohol than a monoside but was unaffected by alkaline hydrolysis. Probably due to enzymatic hydrolysis.

11 See Table 2.

12 Probably a normal anthocyanidin but no definite results could be obtained due to persistent contamination by other substances in the extract. The ferric test appeared negative but was obscured by the presence of tannins, distribution to the cyanidin reagent was zero and to the delphinidin reagent very low, or in most cases, zero. The colour in amyl alcohol at neutrality was generally very much on the red side and the pigment was not destroyed in the oxidation test. These effects were also observed with extracts in which the anthocyanin content was very low.

13 Dark red hairs on the inflorescence (the flowers are white).

14 From a cultivated tree probably a hybrid with *E. calophylla*, a white flowered species. (The *Eucalyptus* genus forms a large part of the vegetation of Australia but very few of the species have anthocyanin-coloured flowers.)

15 Red insectivorous hairs on the leaves. The flowers are white or pink.

16 The fruit was a berry with a red skin and had at the centre a rubbery sac containing the seeds embedded in a paste of semi-solid blue anthocyanin. The red pigment of the skins was found to be peonidin bioside and the blue pigment cyanidin bioside.

CONSTANCY OF SPECIFIC PIGMENTATION.

In any survey of anthocyanins the tacit assumption is made that the anthocyanin pigmentation of a species is constant irrespective of locality and environment. This cannot always be the case, particularly in variable species and species which have a wide distribution.

In a number of cases we have determined the anthocyanins in two lots of material of the same species which were collected in localities at least 500 miles apart. In some cases also we have re-examined Australian species which were included in previous surveys and which we assume were collected from cultivated plants. The results are summarised in Table 2, and it will be seen that there is considerable variation in the sugar residues. In some cases this may be more apparent than real because of interference by impurities in the plant extracts with the tests for glycoside type. This applies particularly to the distinction between dimonosides and biosides. Also Lawrence *et al.* (1939) have pointed out that impurities may cause a monoside to behave like a pentoseglycoside. However, the distinction between a dimonoside or bioside on the one hand and a monoside or pentoseglycoside on the other is unmistakable.

TABLE 2.

Comparison of Anthocyanin Content of a Species Collected in Two Distant Localities.

(*a*) Wild Material Only.

Platylobium formosum: Malvidin monoside in two lots of material.

Glossodia major: Delphinidin dimonoside in material from N.S.W. Delphinidin bioside in material from Victoria.

Clianthus Dampieri: Material from both Western Australia and central Australia had pelargonidin monoside in the red petals and cyanidin monoside in the black spot on the standard petals. Lawrence *et al.* (1939) also record pelargonidin monoside with a little cyanidin. The species occasionally varies somewhat in colour.

Indigofera australis: Malvidin monoside+dimonoside in material from N.S.W. Malvidin bioside in material from Victoria (both wild and cultivated).

Glycine clandestina: Malvidin monoside in material from N.S.W. Ferric-positive malvidin bioside in material from Victoria.

(*b*) Wild and Cultivated Material.

Epacris longiflora: Cyanidin monoside in both lots of material.

Prostanthera ovalifolia: Partially methylated delphinidin dimonoside in wild material from N.S.W. Partially methylated delphinidin bioside in cultivated material from Victoria.

Grevillea punicea: Cyanidin monoside in wild material. Lawrence *et al.* (1939) found cyanidin pentoseglycoside.

Convolvulus sepium: Cyanidin dimonoside in wild material. Lawrence *et al.* (1939) found cyanidin monoside. It is to be noted that wild material of *C. sepium* var. *Soldanella* contains cyanidin monoside.

Helipterum Manglesii: Peonidin bioside in wild material. Lawrence *et al.* (1939) found cyanidin dimonoside.

Kennedya coccinea: Peonidin monoside in both lots of material.

K. rubicunda: Peonidin monoside in wild material. Beale *et al.* (1941) found pelargonidin monoside. This difference may not be real and may be due to the difficulty of distinguishing between pelargonidin and peonidin (p. 62).

K. monophylla: Two wild specimens collected in N.S.W. and Victoria and also a cultivated variety all contained malvidin dimonoside. A cultivated form which appeared rather different morphologically contained ferric-positive malvidin dimonoside.

(*c*) Cultivated Material Only.

Graptophyllum Earlii: Pelargonidin monoside in two lots of material.

Eugenia Smithii (fruit): Malvidin bioside in two lots of material.

Callistemon viminalis: Petunidin monoside in two lots of material.

Sterculia acerifolia: Peonidin monoside in two lots of material.

Doryanthes Palmeri: Cyanidin pentoseglycoside in both the flowers and fruit of material cultivated in N.S.W. Cyanidin monoside in material cultivated in Victoria.

Boronia megastima: Partially methylated delphinidin pentoseglycoside with some bioside in material cultivated in N.S.W. Delphinidin bioside in material cultivated in Victoria. (This species is extensively cultivated.)

Swainsona coronillæfolia: The flower coloration of this species is very variable even in the wild. A red form contained a mixture of delphinidin and malvidin dimonoside and a light blue form contained malvidin dimonoside. Beale *et al.* (1941) found delphinidin dimonoside.

In the twenty species examined there are only five, excluding the doubtful case of *Kennedya rubicunda*, in which the anthocyanidin varies with locality or cultivation and in these the variation is only in the degree of methylation and in most cases is slight. On the other hand there is considerable variation in the sugars which is not all due to difficulties of identification.

CORRELATION OF ANTHOCYANIN WITH FLOWER COLOUR.

It is well known that the colour of a flower is determined not only by the anthocyanin that it contains but also by other factors, in particular the pH of the cell sap and copigmentation of the anthocyanin with tannins or white anthoxanthins. Blueing of flower colours, i.e. shifting of the colour towards blue, is caused by copigmentation and also by decreased acidity of the cell saps, which are invariably slightly acidic (Scott-Moncrieff, 1939).

Table 3 shows the numbers of the various types of anthocyanins which were found in flowers of four colour groups, and the proportions are represented graphically in Figure 1. In discussing these results it is assumed that copigmentation is the major factor causing blueing of flower colour. Differences in cell sap pH have not been considered, and may be of only minor importance in wild species since natural selection favours comparatively strongly acid cell sap (Beale, 1941).

The results indicate two trends. Firstly the occurrence of copigmentation increases with the number of sugar and phenolic hydroxyl groups, and to a less extent methoxyl groups, in the anthocyanin molecule. Thus copigmentation

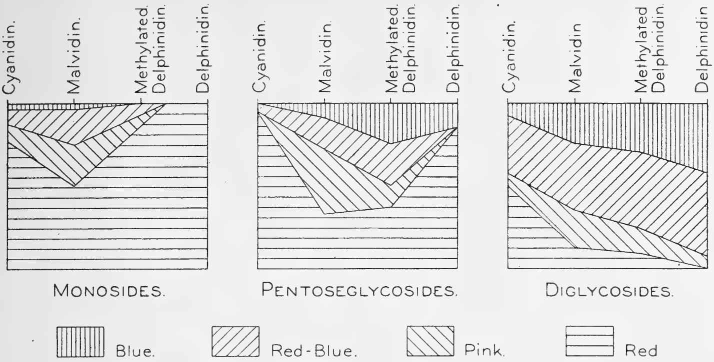

Fig. 1.—Relation between Anthocyanin and Colour.
(Numbers in Table 3 which are too small to have much significance have been excluded.)

TABLE 3.

Relation between Anthocyanin and Flower Colour.

		Red.	Pink.	Red/Blue.	Blue.
Pelargonidin	Diglycosides	2	—	—	—
	Pentoseglycosides	—	—	—	—
	Monosides	2	—	—	—
	Total	6	—	—	—
Peonidin and Peonidin + Cyanidin	Diglycosides	1	1	2	—
	Pentoseglycosides	3	—	—	—
	Monosides	8	—	—	—
	Total	13	1	3	—
Cyanidin	Diglycosides	12	2	8	2
	Pentoseglycosides	16	—	1	—
	Monosides	30	4	4	1
	Total	64	9	14	3
Malvidin	Diglycosides	4	7	12	8
	Pentoseglycosides	4	4	3	1
	Monosides	12	6	5	1
	Total	23	18	25	11
Petunidin and Methylated Delphinidin Mixtures	Diglycosides	1	2	6	4
	Pentoseglycosides	3	1	2	2
	Monosides	5	—	—	—
	Total	10	3	8	8
Delphinidin	Diglycosides	—	2	13	11
	Pentoseglycosides	12	—	—	2
	Monosides	4	1	—	—
	Total	20	3	14	15

Notes to Table 3.

The colour groups are as already defined in the notes to Table 1.

" Diglycoside " includes both 3,5-dimonosides and 3-biosides since these both show the same trends.

" Total " includes in addition to the normal sugar types acylated anthocyanins, mixtures of sugars and indefinite sugars.

The cultivated Australian species have been included.

Species in which the anthocyanin pigmentation is subsidiary to other types of pigments (Class B of Table 1) have been included since a separate analysis indicated that the relationships between anthocyanin and flower colour in these species is virtually the same as in species with flowers entirely pigmented by anthocyanin (Class A).

is much more common in diglycosides than in monosides, pentoseglycosides* being intermediate, and also increases rapidly from pelargonidin and peonidin through cyanidin to malvidin and delphinidin. This effect has been previously recognized (Scott-Moncrieff, 1939). Superimposed on this trend is a second one. The frequency of copigmentation of malvidin, and to a less extent of methylated delphinidin mixtures, relative to that of delphinidin is high in monosides but decreases through pentoseglycosides to diglycosides. This affect applies particularly to the less intense copigmentations, i.e. pink and red/blue, and may be due to a low occurrence of copigmented delphinidin monosides and pentoseglycosides or, more likely, to a high occurrence of copigmented malvidin glycosides.

Whilst the first of these trends appears explicable on physico-chemical lines, the second may be due to genetic factors. Beale, Robinson, Robinson and Scott-Moncrieff (1939) observed that there appears to be a correlation between methylation and copigmentation and that pure methylated types tend to occur with high copigment. Lawrence *et al.* (1939) noted that copigments have a greater effect on malvin that on petunin.

Robinson (1933, 1942) considers that blue pigmentation by an anthocyanin in an acidic cell sap is made possible by the occurrence of the anthocyanin in colloidal solution in the sap, and that the attainment of the colloidal state is aided by the presence of copigments and possibly by protective colloids. On this view the dependence of copigmentation on the number of hydroxyl groups in the anthocyanin molecule can be considered due to the hydroxyl groups effecting association between the molecules and uniting a number of them together to form a colloidal particle, presumably by such mechanisms as hydrogen bonding, dipole association and salt formation. In this connection it may be observed that the tannin and anthoxanthin copigments are themselves polyhydroxy compounds. It appears that seven hydroxyl groups in an anthocyanin molecule (pelargonidin and peonidin monoglycosides) are insufficient to cause any appreciable degree of association or copigmentation, but when the number rises to twelve (delphinidin diglycosides) association is readily effected.

DISTRIBUTION OF THE ANTHOCYANIDIN TYPES.

The data of Table 3 may be condensed to show the proportions of the three anthocyanidin types occurring in flowers of different colours (Table 4). Whilst it cannot be assumed that these proportions, found in Australian flowers, will be the same in flowers of all localities, there is little doubt that the trends illustrated are universal. Thus nearly all blue flowers will contain delphinidin type, the majority of red flowers will contain cyanidin type and the occurrence of pelargonidin will be almost entirely restricted to red flowers. It is apparent therefore

TABLE 4.

Relative Occurrence of the Anthocyanidin Types in Flower Pigmentation.

Colour of Anthocyanin in Flower.	Number of Species.	Pelargonidin %	Cyanidin %	Delphinidin %
Red	134	4·5	57	38
Pink	34	—	26	74
Red/Blue	65	—	29	71
Blue	38	—	10	90

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* As in previous surveys, the term pentoseglycoside indicates a disaccharide sugar residue consisting of a hexose and a pentose.

that the proportion of the three anthocyanidin types found in any survey will be determined by the proportion of red to blue flowers—the "colour ratio"—in the species examined. Table 4 shows general trends only and certain families, e.g. *Myrtaceæ*, may be conspicuous exceptions.

It is possible for the colour ratio, and consequently the distribution of the anthocyanidin types, in a group of cultivated species to differ considerably from the natural colour ratio in wild species. (Variation of the colour ratio in wild species with climate is discussed below.) This position is illustrated by a comparison of the wild and cultivated Australian species collected (Table 5). In this case the preference for red in the artificial selection of the cultivated flowers is very marked, probably because most of the red flowers were large and striking (e.g. *Myrtaceæ*), and for other horticultural reasons.

TABLE 5.

Colours of Species Collected.

	Red.	Pink.	Red/Blue.	Blue.
Wild (219 spp.)	43%	13%	26%	17%
Cultivated (56 spp.) ..	65%	16%	14%	5%

TABLE 6.

Distribution of Anthocyanidins in the Flowers of Australian Wild Species.

	Total Number Examined.	Pelargonidin %	Cyanidin. %	Delphinidin %
Species..	228	1·7	41	62·5
Genera	133	2	47	63
Families	54	5·5	54	78
Orders	41	7	66	83

Notes.

The cultivated Australian species are not included. The New Guinea species are included but approximately 90% of the total number of species are extra-tropical.

TABLE 7.

Distribution of Anthocyanidins in Flowers as Found in Previous Surveys.

(Beale *et al.*, 1941.)

	Total Number Examined.	Pelargonidin %	Cyanidin %	Delphinidin %
Species..	530	19	40	50
Genera	299	23	52	49·5
Families	88	37·5	73	65
Orders	54	44	80	72

Comparison of the distribution of the anthocyanidin types in the Australian wild species (Table 6) with the results of previous surveys (Table 7) shows considerable differences, in particular the more limited occurrence of pelargonidin and the appearance of delphinidin rather than cyanidin as the most widespread anthocyanidin type in the Australian species. These differences might at first sight be considered due to different colour ratios in the two lots of material in which case a high proportion of red in the flowers examined in previous surveys would be inferred. However, this inference is directly opposed to that which may be drawn from comparison of glycoside distributions (p. 65) and degrees of methylation (p. 63).

On the other hand the differences between the two surveys are in accordance with recent genetical findings. Beale (1941) deduced that when an anthocyanin-containing wild type mutates, the direction of mutation is predominantly from delphinidin to cyanidin or pelargonidin, and from cyanidin to pelargonidin, that is from the more to the less oxidised anthocyanidin. Also, mutant types were found to be recessive. In cultivated plants the mutants have a much greater chance of survival, due to artificial selection and breeding of new types, than they have in the wild, where they are usually less viable than the normal types. It follows that cultivation should increase the occurrence of pelargonidin and cyanidin at the expense of delphinidin. Comparison of Tables 6 and 7 indicates that this is the case.

In ascribing to the effects of mutation and artificial selection the differences between the two surveys the assumption is of course made that were it not for this factor the Australian flora examined would be comparable in respect to anthocyanin distribution with the flora examined in the previous surveys. To what extent this assumption is justifiable is not certain in view of the special nature of the Australian flora, which is generally regarded as having been evolved in an intense struggle for existence with consequent great importance of floral pigmentation. It may be noted, however, that the group of families examined in each of the two surveys is much the same.

In the case of pelargonidin the difference between the two sets of figures in Tables 6 and 7 is very striking. Moreover of the six species found to contain pelargonidin (four in the wild and two in the Australian cultivated flowers) most were tropical or sub-tropical species. Thus pelargonidin is a very rare anthocyanidin in temperate Australian plants. The much more frequent occurrence in garden flowers is no doubt due to the fact that it can arise by mutation from both of the other anthocyanidin types, and may also be due to preference for red and orange-red shades. Lawrence *et al.* (1939) noted that many of the flowers which they found to contain pelargonidin originated from tropical or sub-tropical countries. We have found that although the proportion of pelargonidin is higher in tropical and sub-tropical flowers than in temperate flowers (Table 11) it is still very low.

The occurrence of pelargonidin recorded may possibly be slightly less than is actually the case since the distinction between pelargonidin and peonidin in the identification of anthocyanidins is not very definite. However, peonidin is well differentiated from the rest of the anthocyanidins and only eight occurrences of peonidin (not mixed with cyanidin) were found in the wild species and three in the cultivated species. Some of these may have actually been pelargonidin, but even if they are all counted as pelargonidin its occurrence in the wild species rises to only 5%.

A graphical representation (Figure 2) of the figures of Tables 6 and 7 reveals three points of interest: the predominance of delphinidin in the wild flowers, the similarity in shape of the two delphinidin graphs, and the comparative steepness of the cyanidin graph in the garden flowers. Such graphs are not likely to be greatly modified if a larger number of species is examined.

The approximate equivalence of the proportions of delphinidin-containing genera and species in the two delphinidin graphs appears significant. Lawrence *et al.* (1939) considered that this effect was artificial and due to preference for the extremes of colour in artificial selection. This cannot be the case, for the effect appears in the wild flowers.

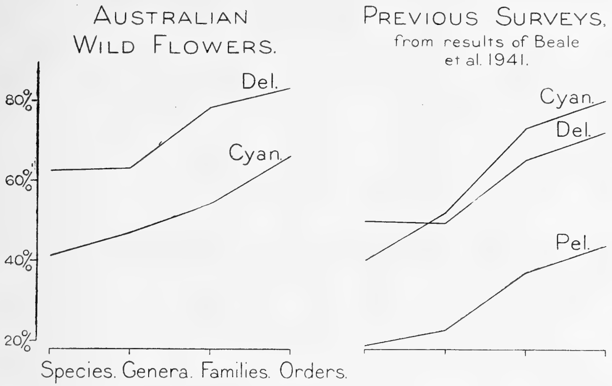


Fig. 2.—Distribution of Anthocyanidin Types.

METHYLATION.

The degree of methylation of cyanidin or delphinidin may be defined as the ratio of the number of occurrences of methyl derivatives (including mixtures due to incomplete methylation) of cyanidin or delphinidin to the total number of occurrences of cyanidin or delphinidin type. In Table 8 the degree of methylation of cyanidin and delphinidin in the previous surveys and the Australian wild species is compared. The term "methylated delphinidin" is used to denote mixtures of the methyl derivatives of delphinidin, or partially methylated

TABLE 8.

Degree of Methylation.

	Australian Wild Flowers (228 spp.).		Previous Surveys* (382 spp.).	
	Number.	%	Number.	%
Peonidin	8	*3·5*	7	*2*
Peonidin + cyanidin	5	*2*	—	—
Cyanidin	80	*35*	139	*36*
Degree of methylation of cyanidin	13/93	*14*	7/146	*5*
Malvidin	66	*29*	74	*19*
Methylated delphinidin	23	*10*	7	*2*
Petunidin	4	*2*	10	*2·5*
Delphinidin	49	*21·5*	109	*28·5*
Degree of methylation of delphinidin	93/142	*65·5*	91/200	*45·5*

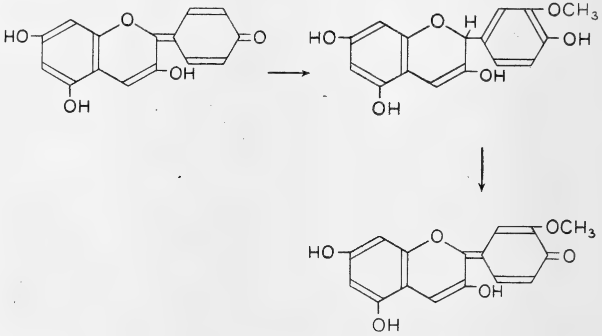
* Figures taken from the results of Lawrence *et al.* (1939).

delphinidin. Ferric positive malvidin has also been included under this heading since there seems little doubt that in the great majority of cases the positive ferric test is due to the presence of small amounts of delphinidin and (or) petunidin though there is the possibility that in some cases it may be due to cyanidin.

The higher degree of methylation in the wild species suggests that cultivation preserves mutations from methylated to unmethylated types. It has already been shown that methylation varies somewhat with locality and cultivation (Table 2). On the other hand the difference in the figures might be considered due to different colour ratios in the two lots of flowers examined. However, it should be noted that in the cultivated Australian flowers (Table 9) the degree of methylation of delphinidin (85%) is even higher than in the wild flowers. This is due to the much higher proportion of red colorations in the cultivated flowers, which results in a decreased proportion of unmethylated delphinidin. It appears therefore that the results of previous surveys, showing a lower degree of methylation of delphinidin than in the wild flowers, do not reflect any undue predominance of red colorations (cf. p. 62).

Little is known of the factors controlling the formation of methylated anthocyanins. It has previously been assumed (Lawrence *et al.*, 1939) that methylation simply involves one additional stage, not necessarily the last stage, in the synthesis of the anthocyanin. The occurrence of mixtures due to partial methylation of cyanidin and delphinidin supports this view. An excellent example is afforded by the fruit of *Smilax timorensis*, which at its centre contains a paste of cyanidin bioside, but in which the skin is pigmented by peonidin bioside.

However, it seems possible that another way in which methylated derivatives may arise is by the addition of methyl alcohol to the quinonoid colour base form of the anthocyanin, followed by oxidation. For example, pelargonidin would yield peonidin. Whilst no direct evidence can be adduced in support of such a process, it may be pointed out that methylation of the 4′-hydroxyl group does not occur.



Cultivated Species.

The results for the cultivated flowers of 56 Australian species are listed in Table 9. A number of Australian species which were examined in previous surveys have been included. Compared with the results for the wild flowers, the cultivated flowers show an increase in the proportion of cyanidin and pelargonidin at the expense of delphinidin, and also an increase in the degree of methylation of delphinidin. These increases result from the artificially large ratio of red to blue flowers discussed above (p. 61). It is considered that the anthocyanin content of these species (most of which were collected from Botanical Gardens) has been very little affected by the preservation of mutants in horticulture since they have been cultivated for a shorter period and on a smaller scale than plants in most other countries.

TABLE 9.

Distribution of Anthocyanidins in Cultivated Australian Flowers.

	Number.	%		Number.	%
Pelargonidin	2	*3·5*	Pelargonidin Type ..	2	*3·5*
Peonidin	3	*5·5*			
Peonidin + cyanidin ..	1	*2*			
Cyanidin	25	*45*	Cyanidin Type	29	*52*
Malvidin	13	*23*			
Methylated delphinidin ..	6	*11*			
Petunidin	4	*7*			
Delphinidin	4	*7*	Delphinidin Type ..	27	*48*

Degree of methylation of cyanidin = 4/29 = 14%
Degree of methylation of delphinidin = 23/27 = 85%

DISTRIBUTION OF GLYCOSIDE TYPES.

In view of the relationships between anthocyanin and flower colour illustrated in Figure 1 it is to be expected that the distribution of glycoside types, like the distribution of anthocyanidins, will be largely dictated by the biological value of the flower colorations.

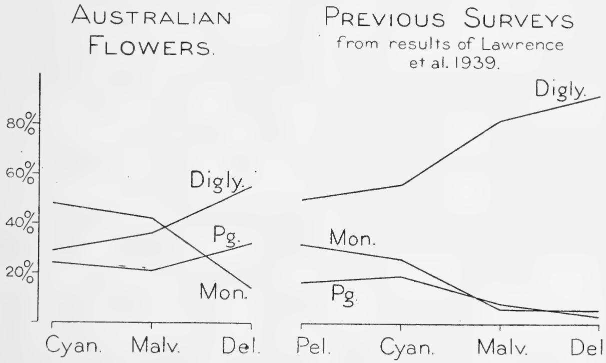


Fig. 3.—Distribution of Glycoside Types.

Comparison between the two sets of results in Table 10 and Figure 3 shows a much lower proportion of diglycosides in the Australian species. As in the case of the anthocyanidins the reasons for this difference might be either mutation, operating in the sense monoside wild type→diglycoside mutant, or different colour ratios in the two sets of material. If the latter were the case the high proportion of diglycosides in the results of Lawrence *et al.* would indicate a much higher proportion of blue colorations in the material examined by them than in the Australian species. (It may be taken that the relations between anthocyanin and flower coloration illustrated in Figure 1 hold also in general for cultivated flowers.) However this is directly opposed to the inference drawn from a comparison of the distribution of the anthocyanidin types (p. 62). It seems, therefore, that the differences between the two surveys in respect to the distribution of anthocyanidin and glycoside types and also degree of methylation cannot be due to any differences in the colour ratios of the two lots of material.

TABLE 10.

Distribution of Glycoside Types.

(*a*) Australian Species.

	Cyanidin (86 spp.). %	Malvidin (76 spp.). %	Delphinidin (44 spp.). %
3,5-Dimonosides	10	24	34
3-Biosides	16	9	18
Total Diglycosides	*29*	*37*	*55*
3-Pentoseglycosides ..	24	21	32
3-Monosides	48	42	14

(*b*) Previous Surveys. (From data of Lawrence *et al.*, 1939.)

	Pelargonidin (71 spp.). %	Cyanidin (139 spp.). %	Malvidin (74 spp.). %	Delphinidin (109 spp.). %
3,5-Dimonosides	30	34		
3-Biosides	20	14	Mostly 3,5-	dimonosides
Total Diglycosides	*51*	*56*	*82*	*92*
3-Pentoseglycosides	17	19	8	3
3-Monosides	32	26	7	5·5

Notes.

The term "diglycoside" includes both 3,5-dimonosides and 3-biosides.

The Australian cultivated species are included. These have the effect of slightly increasing the predominance of monoglycosides due to the high proportion of red colorations.

Mixtures of sugars and indefinite glycoside types are excluded.

The figures include acylated glycosides of the type anthocyanidin-sugar-acyl group but not those of the type anthocyanidin-acyl group-sugar since in the latter case the glycoside type is not determined.

The genetics of factors controlling glycoside differences is at present not known with any certainty (Beale, 1941).

VARIATION OF ANTHOCYANIDIN TYPE WITH CLIMATE.

It was observed by Lawrence *et al.* (1939) that many of the flowers which they found to contain pelargonidin originated from tropical or sub-tropical countries. These authors also suggested that delphinidin appeared to predominate in alpine regions. These trends were clearly illustrated by Beale *et al.* (1941), who classified all the plants which had been examined into tropical, sub-tropical and temperate (including alpine) species.

We have similarly classified the eastern Australian species (Table 11) on the basis of the distributions set out in Table 1 and apart from the very low proportion of pelargonidin and the higher proportion of delphinidin already discussed the effect of climate on the occurrence of the anthocyanidin types is clearly in accordance with the earlier findings (Figure 4).

TABLE 11.

Variation of Anthocyanidin Type with Climate.

	Tropical (43 spp.). %	Sub-tropical (42 spp.). %	Temperate (135 spp.). %
Pelargonidin	7	2·5	0·8
Cyanidin	48	48	35
Delphinidin	43	50	65

Notes.

"Tropical" includes the New Guinea species, the tropical Queensland species and the species which range from tropical to sub-tropical.

"Temperate" includes mainly the species which range from sub-tropical to temperate together with the species restricted to the range of latitude 33°–36° S, and some truly temperate species.

The Western Australian species and species with a very wide distribution are not included. The cultivated Australian species are included.

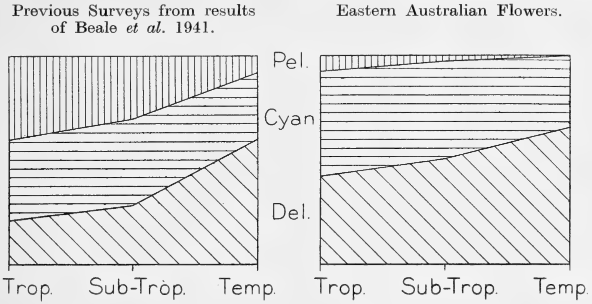


Fig. 4.—Variation of Anthocyanidin Type with Climate.

It should be noted that the plants that we have classified as temperate occur on the sub-tropical side of the temperate zone and include no alpine flora, so the sharp increase in delphinidin in truly temperate species observed by Beale *et al.* is not questioned.

Beale *et al.* found that tropical flowers were redder than flowers of other climates and pointed out that the effect of climate on the distribution of anthocyanidin types is biological rather than chemical. That is, the difference in anthocyanidin distribution is simply the result of different colour ratios in the flowers of different climates. Red pigmentations have a higher biological value than blue in the tropics and sub-tropics but in temperate and alpine climates the value of red apparently decreases and (or) the value of blue increases. There will be several factors controlling the colour ratio in any particular area, the most immediate factor undoubtedly being the colour response of insects and birds.

(Cf. Lawrence and Price, 1940.) It seems likely that the high value of red pigmentations in the tropics is due to the favourable contrast with the pervading green background.

DISTRIBUTION OF ANTHOCYANINS IN FRUITS.

In Table 12 are shown the distributions of anthocyanidins in the fruits of 56 Australian species, of which 85% were wild and, for comparison, the combined results of previous surveys (from the data of Lawrence *et al.*, 1939, and Beale *et al.*, 1941).

TABLE 12.

Distribution of Anthocyanidins in Fruits.

	Australian Species.		Previous Surveys.	
	Number.	%	Number.	%
Pelargonidin	2	*3·5*	9	*16*
Peonidin	2	*3·5*	2	*3·5*
Peonidin+cyanidin	2	*3·5*	—	—
Cyanidin	26	*46*	29	*53*
Malvidin	11	*20*	8	*15*
Methylated delphinidin	2	*3·5*	—	—
Petunidin	—	—	1	*2*
Delphinidin	11	*20*	6	*11*
Total	56		55	
Pelargonidin Type	2	*3·5*	9	*16*
Cyanidin Type	30	*54*	31	*56*
Delphinidin Type	24	*43*	15	*27*
Degree of Methylation :				
Cyanidin	4/30	*13*	2/31	*6·5*
Delphinidin	13/24	*54*	9/15	*60*

It will be seen that, as in the case of the flowers, in the Australian species there is a much lower proportion of pelargonidin and a higher proportion of delphinidin type compared with the results of previous surveys. In this case it does not appear justifiable to consider reasons for the difference in view of the small numbers and the fact that the two sets of figures cover, for the most part, different groups of families.

The distribution of anthocyanidins in fruits appears to depend on climate in the same way as in flowers. Thus eight anthocyanidins of delphinidin type were found in 13 species classed as temperate, while only three were found in 21 tropical species. Also, the two pelargonidin-containing fruits were both tropical species.

In eight cases we have examined both the flowers and fruits of a species and in each case the same anthocyanidin was found in both, though in some cases the glycoside types were different.

NITROGENOUS AND ABNORMAL ANTHOCYANINS.

Most of the species listed in Table 1 as containing nitrogenous anthocyanins have already been recorded in previous surveys. The only new species recorded are *Mesembryanthemum æquilaterale* and *Atriplex cinerea.* Nitrogenous anthocyanins have previously been found in other species of both of these genera

(Lawrence *et al.*, 1939). Two other species, *Veronica Derwentia* (252)* and *Solanum aviculare* (250) were found to contain unstable pigments which may have been nitrogenous. It is noteworthy that these belong to orders placed close together in Hutchinson's classification but far removed from the orders known to contain nitrogenous pigments.

No definite indications were found of the occurrence of non-nitrogenous abnormal anthocyanins. In a number of cases indefinite tests were found to fit into a single pattern and were undoubtedly due to interference by other substances in the plant extract. (See note 12 to Table 1.)

MIXTURES OF ANTHOCYANIDINS.

Mixtures of anthocyanidins due to incomplete methylation have already been discussed. In addition to these, thirteen species (included in Table 1) were found to contain mixtures of anthocyanidins of different type in comparable proportions. The classes of mixtures found were as follows:

Cyanidin + pelargonidin	1
Cyanidin + malvidin	6
Cyanidin + delphinidin	5
Cyanidin + a nitrogenous anthocyanin	1

We would not feel justified in drawing any conclusions concerning biosynthesis of anthocyanins from these data. However, the occurrence of a small amount of cyanidin (which may have arisen from a leuco-anthocyanin) with the nitrogenous anthocyanin of *Mesembryanthemum æquilaterale* (55) is interesting and appears to be the first instance recorded of such a mixture.

SUMMARY.

Following on previous surveys by English workers of the occurrence of anthocyanin pigments in flowers a survey has been made of anthocyanins in the flowers of some 300 native Australian species together with a smaller number of fruits.

The results differ from those of the previous surveys in the distribution of the three anthocyanidin types (pelargonidin, cyanidin and delphinidin), the frequency of methylation of these anthocyanidins and the distribution of glycoside types. These differences are tentatively ascribed to the presence of mutant forms in the cultivated plants examined in the previous surveys. Mutation, together with artificial selection, apparently has the effect of increasing the occurrence of pelargonidin and cyanidin at the expense of delphinidin and also the occurrence of diglycosides at the expense of monoglycosides. The same factors may also increase the frequency of methylation.

The variation in the distribution of the anthocyanidin types with climate and also the correlations between anthocyanin and flower colour found in the earlier work are substantiated. The extent of blueing of flower colour appears to depend on the number of hydroxyl groups in the anthocyanin molecule.

Variation of the anthocyanin pigment of a species with locality is limited and is almost entirely restricted to variation in the type of glycoside and the degree of methylation.

ACKNOWLEDGEMENTS.

We wish to thank Dr. J. R. Price for his valuable criticism of the manuscript and Mr. S. Smith-White and Dr. H. N. Barber for advice on the genetical aspects. For identification of the plant material and advice on the classification we are

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* Hutchinson's number for the family is given to facilitate reference to Table 1.

indebted particularly to Mr. O. D. Evans and to the staff of the National Herbarium, Sydney. We wish to thank also the Directors of the Botanic Gardens of Sydney, Melbourne and Brisbane for provision of most of the cultivated species.

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THE ESSENTIAL OIL OF A PHYSIOLOGICAL FORM OF *BORONIA LEDIFOLIA* (GAY).

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and F. R. MORRISON, A.A.C.I., F.C.S.
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Manuscript received, March 17, 1948. Read, May 5, 1948.

The botany of *Boronia ledifolia* (Gay), a small, erect Rutaceous shrub with bronze green leaves and deep pink flowers, is described in Bentham's "Flora Australiensis", Vol. 1, page 314. Varieties are also described, e.g. *triphylla* and *rosmarinifolia.*

Boronia ledifolia (Gay) is widely distributed, extending from Port Jackson, N.S.W., to central Queensland. The Queensland plant is mostly var. *rosmarinifolia.*

During a visit to Grafton, N.S.W., in September, 1941, Mr. J. Pocock of The Punchbowl directed our attention to a strongly scented Boronia, from which he had distilled some oil. A cursory examination of the leaves and terminal branchlets of this attractive shrub confirmed Mr. Pocock's observations. The overpowering aroma, resembling the constituents of oil of Rue, differentiated this Boronia, which superficially resembled *B. ledifolia* (Gay) from any similar Boronias previously examined by us.

We have since examined the foliage of *Boronia ledifolia* (Gay), *B. ledifolia* var. *triphylla* and *B. ledifolia* var. *rosmarinifolia*, but their lower contents of oils of dissimilar composition readily differentiated the Boronia at The Punchbowl, via Grafton, N.S.W.

No doubt morphological differences will subsequently be noted, but pending further botanical investigation we prefer to call this Boronia *B. ledifolia* variety "A", particularly in view of the reports received from our botanical colleagues, Mr. C. T. White, F.L.S., Government Botanist, Brisbane, Q., and Mr. R. H. Anderson, Chief Botanist and Curator, Botanic Gardens, Sydney.

Both botanists expressed the opinion that our specimens were *Boronia ledifolia* (Gay), but Mr. White added this note, viz.:

> "Your plant in some ways is intermediate between *B. ledifolia* and the variety *rosmarinifolia. Boronia ledifolia*, like *B. pinnata*, is one of those species of which there are a great many forms which may be treated as species, though some run into one another, and the group is a particularly difficult one."

Through the courtesy of Mr. J. Pocock, who provided not only the original specimen of oil but also several consignments of leaves and terminal branchlets, we were enabled to investigate the chemical nature of the essential oil. The whole of the material received at intervals during the past seven years was collected from the one locality near Grafton, N.S.W., where it occurs somewhat sparsely. Efforts to obtain larger quantities of foliage in order to determine the minor constituents of the oil were frustrated by bush fires.

THE ESSENTIAL OILS.

The essential oils obtained from the various consignments enumerated in the accompanying table were of a very pale lemon tint, and possessed the characteristic odour of the principal constituents, methyl n. heptyl ketone and methyl n. nonyl ketone. These two substances constitute about 75% of the oil, the unidentified substances being most probably α-pinene, sesquiterpenes and the methyl ester of anthranilic acid.

The essential oils obtained from *Boronia ledifolia* (Gay) and *B. ledifolia* var. *triphylla* differ markedly both in yield of oil and in chemical composition, from the essential oil derived from the physiological form collected at The Punchbowl near Grafton, N.S.W.

Although these samples were too small for a detailed chemical examination (they measured 8 mls.), preliminary tests confirmed the presence of terpenes and sesquiterpenes and the absence of the characteristic constituents of *B. ledifolia* (Gay) var. "A".

EXPERIMENTAL.

The 160·5 lb. weight of leaves and terminal branchlets yielded on distillation with steam, crude oils, which on examination gave the chemical and physical characters shown in accompanying table. Similar constants have been included for oils obtained from *B. ledifolia* (Gay) and *B. ledifolia* var. *triphylla* for comparative purposes.

All distillates were subjected to repeated fractional distillation, usually at 10 m.m., but only one is recorded, viz. 1/9/1947. The crude oil was distilled through a 60 cm. Vigreux column with a Weir reflux head at total reflux, with intermittent take-off.

Fraction.	b.p.	Pressure.	Bath. Temp.	Vol. ml.	$d\frac{15°}{15}$	$\alpha_D^{20°}$	$n_D^{20°}$
1	178°	770 mm.	278°	6·5	0·8476	+10·72°	1·4436
2	185°	,,	283°	8·0	0·8420	+6·4°	1·4365
3	189–190°	,,	290°	6·0	0·8364	+3·0°	1·4290
4	79°	10 mm.	196°	14·0	0·8299	+0·25°	1·4228
5	88°	,,	244°	8·0	0·8299	±0	1·4230
6	104°	,,	272°	15·0	0·8367	±0	1·4311
Residue					0·9050	±0	1·4730

DETERMINATION OF THE KETONES.

A carbonyl estimation on the crude oil showed the presence of about 72–75%, calculated as methyl n.-nonyl ketone.

Identification of Methyl n.-heptyl ketone.

Fraction 4 (1 ml.) on treatment with semicarbazide hydrochloride reagent gave a white crystalline precipitate in good yield. On recrystallisation from boiling aqueous alcohol, flat, rhomboidal monoclinic crystals were obtained melting at 119–120° C.

TABLE 1.

Boronia ledifolia (Gay) Variety " *A* ".

Date.	Locality.	Weight of Leaves.	Yield of Oil.	$d\frac{15^\circ}{15}$	$\alpha_D^{20^\circ}$	$n_D^{20^\circ}$	Ester No. 1½ Hours Hot Sap.	Solubility in 70% Alcohol W/W.	Remarks.
17/ 9/1941	The Punchbowl, near Grafton, N.S.W.	Sample of oil.		0·836	−0·03°	1·4289	23·5	*Vol.* 1·0	Oil distilled and submitted by Mr. J. Pocock.
26/11/1941	,, ,, ,,	40 lb.	0·12%	0·8354	−1·54°	1·4266		1·0	Distilled by Mr. J. Pocock. Yield considered low through dry conditions and plant past flowering.
11/11/1942	,, ,, ,,	18 lb.	0·46%	0·852	−0·75°	1·4341		1·0	Plants in full flower and very good condition.
2/ 8/1946	,, ,, ,,	23 lb.	0·19%	0·8511	Inactive	1·4375		1·0	
1/ 9/1947	,, ,, ,,	79½ lb.	0·23%	0·8448	+2·88°	1·4364		1·0	
Boronia ledifolia var. *triphylla.*									
13/ 8/1947	National Park, near Sydney.	29 lb.	0·06%	0·9080	+22·3°	1·4850		*Insol.* 10 vols. 80% alcohol, W/W.	Collected by S. Smith-White. Fresh leaves and terminal branchlets. Plants profusely flowering.
Boronia ledifolia (Gay).									
16/ 1/1948	Cowan, N.S.W.	29 lb.	0·06%	0·9130	+27·2°	1·4819		*Insol.* 10 vols. 80% alcohol, W/W.	Whole plants collected by S. Smith-White and H. H. G. McKern.

Found: C, 59·84; H, 10·6; N, 20·93. Calculated for $C_{10}H_{21}ON_3$,: C, 60·24; H, 10·62; N, 21·09.

On treatment of 1 ml. with 2 : 4 dinitro-phenyldrazine reagent, yellow flakes were obtained in good yield, which on recrystallisation from aqueous alcohol melted at 57–58°.

Found: C, 55·32; H, 6·82; N, 17·27. Calculated for $C_{15}H_{22}O_4N_4$: C, 55·86; H, 6·75; N, 17·39.

These results, together with the physical constants, show the ketone to be identical with methyl n.-heptyl ketone.

Identification of Methyl n.-nonyl ketone.

Fraction 6 (1 ml.) on treatment with semicarbazide hydrochloride reagent gave a good yield of crystalline semicarbazone, of melting point 122–123°. A mixed melting point determination with an authentic sample semicarbazone of methyl n.-nonyl ketone gave the same result.

Found: C, 63·09; H, 11·12; N, 18·30. Calculated for $C_{12}H_{25}ON_3$: C, 63·37; H, 11·08; N, 18·47.

The 2 : 4 dinitro phenylhydrazone was also prepared. On recrystallisation from aqueous alcohol, the crystals melted at 62–63° C. A mixed melting point determination with an authentic sample of the 2 : 4 dinitro phenylhydrazone of methyl n.-nonyl ketone showed no change of melting point.

UNIDENTIFIED CONSTITUENTS.

Owing to the limited quantity of oil available, it was not practicable to isolate the minor constituents. Redistillation of fraction 1 gave 2 mls. of oil (b.p. 146–162, $d\frac{15^\circ}{15}$ 0·8525, $\alpha\frac{20^\circ}{D}$ +16°, $\frac{20^\circ}{D}$ 1·4521) which probably contained α-pinene. The presence of sesquiterpene was indicated by the formation of a purple colour by the action of bromine vapour on solution of the residual fraction in glacial acetic acid. The residual fraction exhibited strong fluorescence under ultra-violet light, and possessed the characteristic odour of methyl anthranilate. Efforts to isolate the ester were not successful.

ACKNOWLEDGEMENTS.

Our thanks are due to Mr. J. Pocock, of The Punchbowl, N.S.W., for bringing this Boronia and its essential oil under our notice, and for supplying leaves and terminal branchlets for subsequent investigation.

We are also indebted to Miss J. Fields, of the Organic Chemistry Department of the University of Sydney, for the micro-combustion results, and to our assistants, Mr. H. H. G. McKern, A.A.C.I., and particularly Mr. K. G. O'Brien, B.Sc., for much valuable help in completing the investigation.

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Part II

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SPECTROSCOPIC ANALYSIS OF ALLOY STEELS.

By C. JAMES,
The Commonwealth Steel Co., Waratah.

Communicated by S. C. BAKER.

With Plate VII and one text-figure.

Manuscript received, April 23, 1948. Read, June 2, 1948.

Schliebmann (1934) and Emery (1941) have published details of visible spectrum lines employed for qualitative spectroscopic analysis of steels. The spectra of the high alloy steels manufactured by the Commonwealth Steel Co. differ considerably from these and from the charts supplied by Adam Hilger Ltd. with the " Spekker " Steeloscope, which may be described as a spectroscope with two large prisms in tandem having ample resolution for ferrous work in the visible region of the spectrum and robust enough for use on a steel plant.

Approximately 130 alloy steels are manufactured by the Commonwealth Steel Co. and about half of these can be positively identified with the Steeloscope alone; the remainder can be classified into groups. Typical analyses of three main types of steels are given in Table I. The spectroscopic examination is mainly a final check against mixed bars before shipment; it is also used for qualitative work such as the identification of a " lost " bar. The success of the Steeloscope depends largely on the skill and experience of the operator but the principles of the identifications can be seen from a study of Table I. Thus only F2 contains titanium; only B1 contains cobalt, etc. Then again only a few steels contain molybdenum and this is usually in conjunction with nickel and

TABLE I.

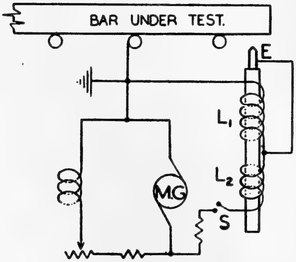
Typical Analysis of Main Types of Alloy Steels.

Grade.	C.	Si.	Mn.	P.	S.	Ni.	Cr.	Mo.	W.	Va.	Co.	Ti.
	%	%	%	%	%	%	%	%	%	%	%	%
P10	0·9–1·1	0·80 max.	11·0–13·5	0·075	0·04	3·5–4·5	0	0	0	0	0	0
F2	0·14 max.	0·5–0·8	0·6–0·80	Low	Low	9·50–10·50	17·5–18·5	0	0	0	0	0·5–0·8
B1	0·78–0·84	0·30 max.	0·40 max.	0·020	0·020	0	4·2–4·7	0	21·0–22·0	1·0–1·5	11·5–12·5	0

chromium. Further separation is achieved by the quantitative estimations detailed below. On an average day one operator examines about 800 bars for the presence or absence of at least nickel, chromium and molybdenum.

Operating Technique.

The bars, billets and blooms in sizes varying from $\frac{3}{8}$ in. to 7 in. round or square with average length about 15 feet are brought to the Steeloscope by overhead crane direct from processing and placed on an elevated table. From there each bar is placed in turn on rollers in a channel leading to the arc unit, which is illustrated by the diagram. Essentially the arc unit consists of a pair of vertical solenoids, L_1 and L_2, having a common iron armature to which a $\frac{3}{8}$ in. Armco iron electrode, E, is attached; this is the live electrode and is negative; it is directly beneath the bar under test. When the magnetically operated push button switch, S, is closed, both solenoids are energized, causing E to contact the bar, thereby short-circuiting L_1, so that E drops a short distance thus striking the arc. Suitable limit resistances are included to give an arc current of 8 amperes. Power is supplied by a motor-generator set, MG, delivering 240 volts D.C. Thus the operator merely presses S to strike the arc, and handling is very rapid.



Circuit Diagram. of Arcing Table.

Spectrum Lines Employed.

Most of the work is done in the 4708A to 4719A section of the spectrum because this enables the determination of the main elements without moving the eyepiece of the Steeloscope; the lines used are listed in Table II and are shown in the Plate. When present molybdenum is always estimated with the "confirmative" line 5533A because of the closeness of Mo 4717·9 and Cr 4718·5. Nickel is frequently difficult and the presence of scale and oil on the bar make it desirable to check the estimation with the Ni 5081 "confirmative" pair.

Table II.

Spectrum Lines Employed.

4708–4719A Lines.	Confirmative Lines.	Other Elements.
Cr 4708·04 and 4718·45	Mo 5533·0	Co 4867·9
Mo 4717·92	Ni 5080·5 and 5081·1	Ti 4533
Mn 4709·7		Va 4408·52
Ni 4714·42		W 5514

Vanadium, tungsten, titanium and cobalt are checked individually with the lines headed " Other elements " in Table II; they are marked in the Plate.

Carbon steels present difficulties when the alloy constituents do not vary and the carbon does. In such cases the carbon can be estimated by the colour and form of the sparks thrown from a small high-speed grinding wheel pressed against the bar.

The silicon lines used by Schliebmann do not appear with the concentrations and set-up employed here; unfortunately, too, silicon throws a spark from the grinder that is indistinguishable from that of low concentration tungsten. Thus silicon is the only important element that cannot be estimated with the Steeloscope.

QUANTITATIVE ESTIMATIONS.

Chemical checks have shown that an experienced operator can make certain quantitative estimations with a fair degree of certainty using the Steeloscope on the works.

The minimum concentrations of the alloy constituents necessary for positive identification are listed in Table III. Thus if, for example, a bar contained 0·5% tungsten, the Steeloscope operator would not see the tungsten line and would record tungsten as absent. Cobalt is not included in this table because low concentrations have not been encountered.

TABLE III.

Minimum Concentration for Identification.

	%		%
Cr	0·05		
Mn	0·10	Ti	0·15
Mo	0·06	Va	0·15
Ni	0·3	W	1·0

Manganese.

The majority of steels contain 0·3% to 0·8% manganese, and by estimating the intensity of Mn 4709·7 it is easy to distinguish 0·3%, 0·5% and 0·8%. A few steels contain up to 12% and these are readily recognized.

Chromium.

The majority of steels contain 0·4% to 1·2% chromium; only Cr 4718·5 appears when there is less than 0·5%, but when the chromium content exceeds 0·5% the Cr 4708·0 line appears and its intensity enables the separation of 0·8% from 1·2%. Other steels contain 14% to 25% chromium and still using Cr 4718·5 one can say whether the concentration is nearer to 14% or to 25%.

Molybdenum.

Only a few steels contain molybdenum, and in these it is quite easy to distinguish 0·1%, 0·2% and 0·3% using Mo 5533.

Nickel.

In nickel steels containing 3% nickel all three of the lines in Table I may look much brighter than in another type of steel containing 8% nickel; but within a given grade 0·3%, 1·5% and 3·0% can be separated using any of the lines in Table II, but the 5081 Ni pair is preferred. When 20% nickel is present the Ni pair are about the same intensity as neighbouring iron lines; over 20%

they are much stronger and under 20% much weaker than the iron lines. Usually, too, high nickel content is associated with high chromium content and *vice versa*, so that a nickel estimation can often be checked by estimating the chromium.

ACKNOWLEDGEMENTS.

I wish to thank the Management of the Commonwealth Steel Co. for permission to publish this paper and the Physics School of the Newcastle Technical College for the use of their Hilger "Wavelength" spectrometer in the selection of the spectrum lines employed and the preparation of the Plate.

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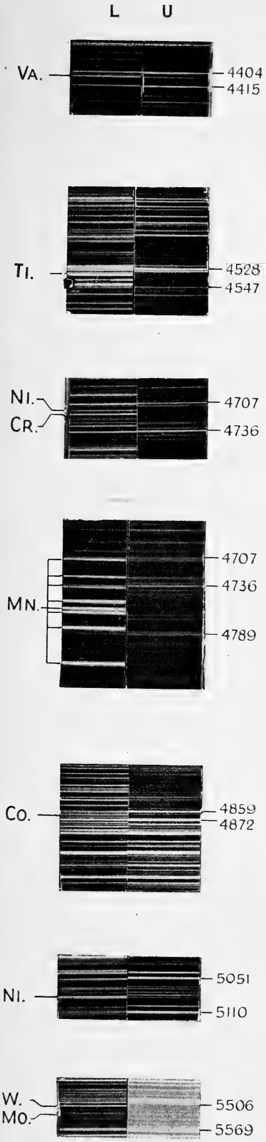
EXPLANATION OF PLATE.

The visible spectra of the three alloy steels of Table I are shown, together with a spectrum of Armco iron, to serve as a wavelength scale.

Sectional enlargements of the analytical spectrum lines, together with the corresponding sections of the iron spectrum, enable the selection of the analytical lines in the spectra of the three steels selected.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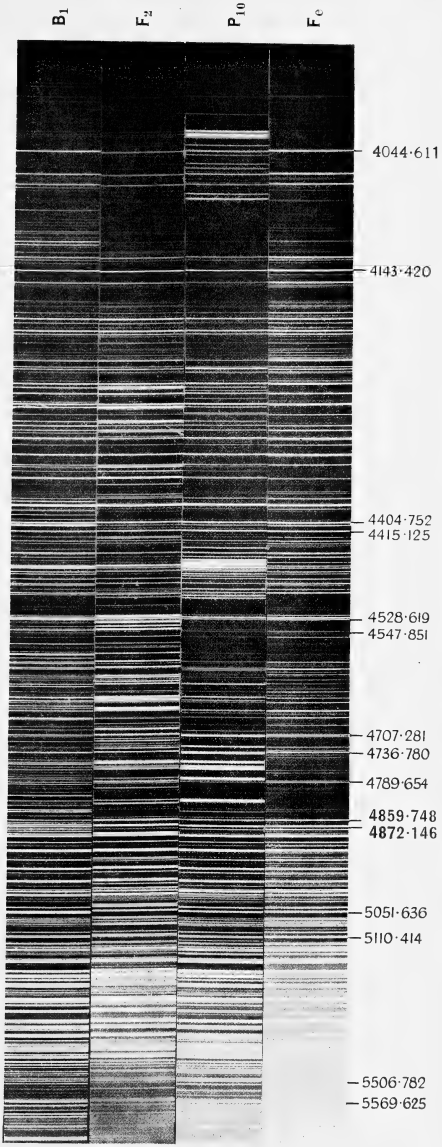

B_1
F_2
P_{10}
F_e
4044·611
4143·420
4404·752
4415·125
4528·619
4547·851
4707·281
4736·780
4789·654
4859·748
4872·146
5051·636
5110·414
5506·782
5569·625

NITROGEN IN OIL SHALE AND SHALE OIL.

I. The Nitrogen Compounds Present in Kerogen.

By Geo. E. Mapstone, M.Sc., A.A.C.I., M.Inst.Pet.

Manuscript received, April 29, 1948. Read, June 2, 1948.

Although oil shale deposits have been exploited for about a century, little is known about the constitution of the organic portion or kerogen of the shales, and even less appears to be known about the origin or nature of the nitrogenous constituents of the kerogen.

Table 1.

Ultimate Analyses of Kerogens.

(Re-calculated to Ash-free Basis.)

Shale.	Australian.				American.				Scottish. Typical.	Estonian.
	Marangaroo Rich.	Joadja Creek.	Glen Davis.	Newnes.	Kentucky.	Colorado.	Utah.	Nevada.		
% C.	84·20	80·6	85·1	81·9	79·0	79·3	80·5	82·3	80·02	77·2
% H.	11·93	12·9	10·6	10·2	8·3	10·5	9·8	8·2	7·65	9·2
% N.	0·31	0·3	1·3	0·8	2·2	2·6	2·7	1·7	2·30	0·4
% S.	1·02	0·3	0·5	0·7	2·3	1·2	1·5	4·3	0·61	2·0
% O.	2·54	5·9	2·5	6·4	8·2	6·4	5·5	3·5	9·42	11·2
Reference	1	2	3	4	4	4	4	4	5	6

The nitrogen content of kerogen varies with and in each deposit and ranges from about one-fifth of one per cent. to nearly three per cent. of the kerogen by weight (Table 1). When the origin and properties of kerogen are discussed the nitrogen-containing materials present are usually overlooked. However, this should not be so, as quite small amounts of nitrogen can be associated intrinsically with quite large amounts of material. For example, a nitrogen content of three per cent. is equivalent to the presence of nearly twenty per cent. of protein matter (see Table 2).

Table 2.

Source of Nitrogen.	Nitrogen Content.	Amount Equivalent to 1% of N.
Chlorophyll *a*	7·1%	14·0%
Chlorine *e* (a degradation product of chlorophyll)	9·4%	10·5%
Protein	16·0%	6·25%

Before we can advance very far in the elucidation of the nature of the nitrogen compounds present in kerogen it is essential that we first review the evidence on the origin and nature of the kerogen itself. The original suggestion of Professor David (7) that the torbanites of New South Wales are of algal origin is now generally accepted. Twenhofel (8) and Dulhunty (9) have suggested that periodic growth of algæ built up layers of organic débris in lakes. After burial this was changed to torbanite by polymerization of the algal substance and the pressure of the overlying sediments. The modern counterparts of such lakes exist in the south-west of Western Australia and in the Coorong district of Victoria in Australia, and in Lake Bal in Siberia.

At this stage it is of interest to note that highly organized plants contain much less nitrogen than the more lowly organized plants. Thus bacteria contain up to 13%, algæ 3·2 to 4·8%, and typical swamp plants about 1·6% nitrogen (10).

Not all oil shales, however, are of algal origin; for example, the shale from Orepuki, New Zealand, " consists mainly of what would appear to be completely macerated plant débris " (11), while the kerogen of Tasmanian oil shale is predominantly a spore material (12). In discussing the origin of petroleum, Wilcox (13) explains the origin of oil shales as buried lake muds in which high molecular weight organic material remains to form some part of the final product of the squeezing and hardening process, during which petroleum may have been expressed. This American viewpoint is of interest owing to the enormous oil shale reserves of the United States of America, most of which are, however, of low grade.

Carlson (14) conceived the structure of the kerogen of the American shales he examined as that of a long chain fatty acid combined with an inorganic base.

Cane (1), working on the torbanites of New South Wales, has extended and combined the theories of Dulhunty and Carlson by suggesting that " kerogen has been formed from fatty acids produced from algal detritus by the removal of carbohydrates and protein matter by bacterial decomposition. The remaining fats are presumed to have been extensively hydrolysed to the free acid." This, however, need not mean that kerogen consists entirely of polymerized fatty acids, or that it is free from carbohydrates and proteins. However, the Carlson-Cane theory of the nature of the kerogen does not account for the presence of nitrogen in the shale except as incidental matter.

From a microscopic examination of the New South Wales torbanites, Dulhunty (15) has described five distinct organic constituents, of which gelosite and retinosite usually occur as minute rounded globules resembling organic cells packed together. The difference between these two constituents appears to be biological rather than environmental (16) and they would presumably be the Carlson-Cane polymerized fatty acid material.

The torbanites of New South Wales are frequently associated with cannel coal, one often changing into the other in the deposit, although the constitution of the two materials is quite distinct (16), the organic constituents of the cannel coal being of vascular plant origin and include spore material, pollen and resin. When cannel coal is closely associated with the torbanite the two are usually mined and retorted together for the production of oil.

Conacher (17) remarks that the nitrogen in the kerogen appears to originate wholly or mainly from the vegetable débris from which the kerogen was formed. The vegetable nature of the nitrogenous constituents of kerogen is supported by the work of Steuart (18), who distilled an artificial shale oil from a mixture of lycopodium dust and Fuller's earth. The oil contained nitrogen compounds and was similar to Scottish shale oil.

The nitrogen compounds present in the vegetable débris, which was the pregenitor of the kerogen, could be of alkaloidal, porphyrinic (chlorophyll) and protein origin.

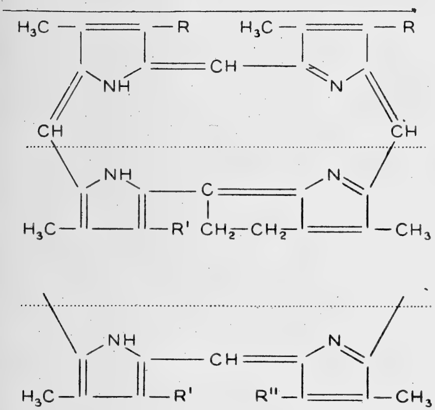
ALKALOIDAL NITROGEN.

Since oil shale is considered to be formed principally as lake muds, etc., the alkaloidal origin of at least the major portion of the nitrogen is immediately precluded as "alkaloids are found almost exclusively in the seed bearing plants" (19). No further consideration is therefore given to this possible, but improbable source, although, since they are more resistant to decay, any alkaloids which may be present would tend to accumulate in the kerogen.

PORPHYRINIC NITROGEN.

Treibs (20, 21, 22, 23) identified porphyrins in a wide range of organic minerals including oil shales, oil slates, cannel and other coals, crude oils, etc.

The porphyrinic material was extracted from the extremely finely divided shale with chloroform, benzene or glacial acetic acid. The extracted material was fractionated by extraction with hydrochloric acid and purified by crystallization or chromatographic adsorption. The porphyrin complexes identified by their absorption spectra were desoxo-phyllerythrin (I), desoxophyllerythro-ætioporphyrin (II), mesoporphyrin (III), meso-ætioporphyrin (IV) and deutero-ætioporphyrin (V). The greatest amount of porphyrin complexes was found in an oil slate from Switzerland which contained 0·34–0·40%. The main complex present in this slate was found to be in the form of a vanadyl complex. Ferric complexes of the porphyrins were found in some Bavarian shales.



I. R $= C_2H_5-$
R' $= -CH_2CH_2CO_2H$

II R $=$ R' $= C_2H_5-$

III. R $= C_2H_5-$
R' $=$ R''
$= -CH_2CH_2CO_2H$

IV. R $=$ R' $=$ R'' $= C_2H_5-$

V R $= -H$
R' $=$ R''
$= -CH_2CH_2CO_2H$

Fig. 1.—Porphyrins Detected in Shales by Treibs (19, 20, 21, 22).

Treibs suggested a mechanism for the formation of these porphyrins from chlorophyll and demonstrated its practicability. By slowly heating pheophytin in petroleum to 250°–320° C. phylloerythrin was obtained, and further heating to 360° C. gave desoxophyllerythro-ætioporphyrin (22), which was the main constituent of the porphyrins isolated from the shales. Although this method employed a relatively high temperature, it is probable that, in the formation of the shales, etc., the reaction was biochemical rather than thermal as the occurrence of the acid porphyrins excludes temperatures of formation greater than 200° C.

Treibs (23) also observed the presence of green pigments associated with the porphyrin complexes and he found that they were present in sapropels, although the porphyrins were absent. It would appear that these pigments consist of chlorophyll and/or its initial degradation products. This suggestion is supported by the observation of Wells and Erickson (24), who reported the presence of chlorophyll in a lake bottom mud.

Pestovskii, Bednyagina and Mikhailova (25) observed that the precursors of thiophenes which appeared on the distillation of some Ural crude oils appeared to have been derived from porphyrins in the crude oil by the conversion of the pyrrole rings into thiophene rings. The mechanism of the change was envisaged to have been due to the presence of hydrogen sulphide from the fermentation of the original organic deposit, and the catalytic influences of the rocks, etc. It is quite feasible that some of the porphyrinic constituents of the kerogen may have been similarly modified to give complex nitrogen- and sulphur-containing materials of the same general structure.

Despite the proven presence of porphyrinic nitrogen compounds in many oil shales, the amounts found to be present have been far from sufficient to account for the high nitrogen content of the kerogens.

PROTEIN NITROGEN.

There is apparently no record in the literature of protein matter or its degradation products having been detected in shale, although the nature of the precursors of the kerogen indicated that proteins were most certainly present in the original deposits. Also it is doubtful whether they were more than partially removed or transformed by the biological processes involved in converting the original algal, spore or other plant material into kerogen.

In general, it appears that the kerogen of shales has probably undergone less biochemical decomposition than the organic constituent of coal. It is therefore of interest to note that a school lead by Terres (26) regards the protein matter of dead microorganisms as an important source material of coal, thus accounting for the relatively constant and high percentage of nitrogen found in coal.

Waksmann (27) has shown that lignin tends to form complexes with proteins. These complexes are highly resistant to plant decay and might well influence the retention of nitrogen compounds in the shale on maturing.

Also, Maillard (28) has found that humus-like compounds were readily obtained by the condensation of sugars with amino acids, a reaction which has been observed to take place at temperatures as low as 37° C.; and these products readily yielded cyclic nitrogen compounds on heating.

Jodidi (29) found amides and mono and diamino acids in peat. Shacklock and Drakeley (30) applied Jodidi's technique to coal with the same results, and found that the amount of nitrogen extractable with boiling dilute acid decreased with increasing rank of the coal.

A long series of nitrogenous compounds including proteins, amino acids, amides, amines, purines, pyrimidines, pyridine derivatives, chitin and nucleic acids has been isolated from soil humus, humic acid preparations and peat and is quoted as proof of the protein nature of the younger fossil fuels (10).

A very small amount of the nitrogen in coal has been shown to be directly attached to a benzene ring by the isolation of 2.4.6 tribrom aniline from the products of the alkaline hypobromite oxidation of coal (31). This could be explained by the oxidative bromination (via anthranilic acid) of tryptophane residues from the protein in the material from which the coal was formed.

Indirect, but also rather inconclusive evidence for the presence of protein in kerogen is that ammonia, which is almost invariably present among the pyrolytic decomposition products of protein (32), is also produced during the entire course of the pyrolysis of kerogen (33), though mainly at the higher temperature (34).

The presence of pyridine derivatives in coal (35, 36) as well as in humus and peat (10) could be explained by the condensation of proteins and amino acids with aldehydes and ketones during the degradation of the original organic material.

The material obtained by ether extraction of Glen Davis torbanite which had been dehydrogenated with sulphur at 150°–155° C. until there was no further evolution of hydrogen sulphide, was a light brown, low viscosity oil with a strong pyridinic odour (37). From the low temperature employed this can probably be taken as evidence of the presence of some pyridine ring systems in this kerogen.

The available evidence concerning the presence of protein material in kerogen is far from conclusive, though it appears that, in the absence of any other likely and abundant source material the bulk of the nitrogen in the kerogen has had its origin as such. The original proteins have probably been extensively modified during the biochemical conversion of the deposits into oil shale by deamination and decarboxylation, and by condensation with aldehydes and ketones, etc., produced during the process. Such modified proteins would be quite insoluble in various solvents, and this is in keeping with the properties of kerogen.

It is obvious that, if any light is to be shed on this problem of the nitrogenous constituents of kerogen, much more work on the subject is necessary. Consideration of the pyrolytic decomposition products of proteins and porphyrins can be expected to give some further but indirect evidence of the nature of the nitrogenous constituents of the kerogen, and will be discussed in a later paper.

SUMMARY.

The nitrogen content of shale kerogens is far from insignificant and appears to be of porphyrinic (chlorophyll) and protein origin. Treibs has identified small amounts of several porphyrins in oil shales but in quantities too small to account for more than a fraction of the total nitrogen present. It is suggested that the bulk of the nitrogen of the shale kerogen is of protein origin and has been extensively modified during the kerogen formation.

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NITROGEN IN OIL SHALE AND SHALE OIL.

II. ORGANIC NITROGEN COMPOUNDS IN SHALE OIL.

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Despite the fact that many workers have examined the organic nitrogen compounds from shale oil, relatively few of the bases have been isolated and positively identified. This has been due mainly to the complex and unstable nature of the materials being handled, and to the fact that ammonia has been the only commercial nitrogenous product obtained from shale.

Primary, secondary and tertiary bases have been detected as classes, while quaternary bases have been suspected but not proved (1). An extensive survey of the literature has failed to reveal the isolation or identification of any primary or secondary amine from shale oil. Of the tertiary amines only pyridine bases have been isolated, though isoquinoline and quinoline homologues have been claimed.

The different classes of bases will be discussed in turn.

PRIMARY AMINES.

Horne, Finley and Hopkins (1) detected only traces of primary amines in the bases from the gasoline fraction of a shale oil by Hoffman's carbylamine reaction.

McKee (2) found only traces of primary amines when investigating the reaction of the bases from De Beque (Colorado) shale oil with nitrous acid.

SECONDARY AMINES.

Almost every investigator who has examined the tar bases from shale oil has obtained positive evidence for the presence of pyrroles as a group.

They are generally detected by means of the pine shaving test, though all general reactions of the pyrrols have been obtained (1, 3, 4). Despite the fact that Williams in 1854 (5, 6) was the first to detect them, the only attempt that appears to have been made to give any more than a cursory examination of this class of bases (1) failed, owing to the crude bases (boiling range 195°–250° C.) decomposing on vacuum distillation to give ammonia, free carbon and tertiary amines.

McKee (3) considered it probable that the higher boiling secondary amines were hydrogenated pyridines, though no evidence was presented to support this view.

In order to test for the presence of hydrogenated quinolines in Tasmanian shale oil, Cane (4) checked the refractive index before and after dehydrogenation of the purified bases with selenium. From his results he deduced that there were no hydrogenated quinolines present. Cane suspected the presence of a piperidine nucleus in the secondary bases, but the dehydrogenation of any piperidines present would have had the same effect in increasing the refractive index as the hydrogenated quinolines so these too must have been absent.

Apparently no dialkyl, alkaryl or diarylamines have been detected in shale oil, so it appears that most, if not all, of the secondary amines present are pyrrole derivatives.

TERTIARY AMINES.

Reference to the occurrence of tertiary bases in shale oil are numerous, but relatively few investigators have succeeded in isolating any of the pure bases.

Different workers have claimed to have identified bases of the pyridine, quinoline and isoquinoline series. The available evidence in each of these classes will be examined in turn.

Because of the very much greater chemical and thermal stability and basic characteristics of these compounds, as compared with the secondary amines present in shale oil, they have been easier to separate from the oil and examine. This explains why the bulk of the work done has been on these compounds.

PYRIDINES.

Williams, in 1854 (5, 6), was the first investigator to isolate and identify pyridine bases in shale oil. From the ultimate analyses of the platinichlorides of the fractionated bases he detected picoline, lutidine, collidine and parvoline. By fractional crystallization of the platinichloride of that portion of the bases boiling below 210° F. he obtained fractions whose platinum content corresponded with the platinichlorides of lutitine, picoline and pyridine. Since this work was carried out well before there was knowledge of the isomeric forms of the higher bases, we can say that the only pure base Williams detected was pyridine.

Garrett and Smythe (7, 8) isolated and examined the bases from the lower boiling fractions of Scottish shale oil and identified pyridine, α picoline, four lutidines and γ collidine. They were unable to identify any of the components of the higher cuts as they could not obtain crystalline derivatives.

Discussing Scottish shale oil, Smith and Peutherer (9) state that " nitrogen present in the shale oil . . . exists mainly as basic compounds such as pyridine and its derivatives."

Horne, Finley and Hopkins (1), working on the oil from an American shale, were unable to isolate pure pyridine by fractional distillation of their basic oil, but they isolated and identified α picoline. Another fraction proved to be β and/or γ picoline, but the identification was not carried further. Lutidine, collidine and parvoline fractions were also obtained and analysed but they did not isolate or identify any pure member of this series.

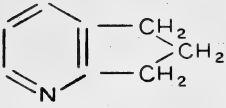
McKee (2) examined the bases from De Beque, Colorado, shale oil and concluded that the bases boiling up to 390° C. were " mostly methylated pyridines and closely related compounds " and not quinolines. The only individual base that he identified was 2.4.6. trimethyl pyridine.

Kogerman (10) examined the bases from Estonian shale oil and, although he classified them as belonging to the pyridine and quinoline series, he did not prove his classification.

Cane (4) isolated and identified 2.4.6. trimethyl pyridine in the bases from a specially prepared crude oil from Tasmanian spore shale.

In a thorough examination of the bases present in Fushun shale oil Eguchi (11, 12, 13) isolated and identified eighteen pyridine homologues though he did not detect pyridine itself. He also isolated a 2.3.6 dimethyl ethyl pyridine but did not establish its full configuration.

Eguchi (13) also isolated a 2,3 disubstituted pyridine with the formula C_8H_9N which he called " pyrindane ". In order to account for its properties he tentatively assigned it the structure



Thompson and Bailey (14) confirmed the structure of this base by synthesis and called it 5.6 dihydro pyrindene.

	Thompson's 5.6 Dihydro-pyrindene.	Eguchi's Pyrindane.
Boiling point	199° C. at 750 mm.	199·8° C. at 761 mm.
Melting point of picrate ..	187° C.	181° C.
Refractive index	1·5407	1·541

This base belongs to a new class of bicyclic nitrogen compounds and appears to be the first of the class to have been obtained from any source.

Dodonov and Soshestvenoskaia (15) examined the bases from a bituminous shale from the middle Volga region. They isolated and identified with certainty pyridine, two picolines and three lutidines.

From De Beque (Colorado) shale oil Stauffer (16) isolated a series of pyridine bases from C_7 to C_{13} and identified 2.4.6 trimethyl pyridine and 2 methyl 5 ethyl pyridine. The iodine numbers of the fractionated bases indicated the presence of some unsaturated side chains.

In recent work at the Oil Shale Research and Development Laboratories of the U.S. Bureau of Mines (17) on the bases present in shale naphtha the ultra-violet absorption spectra, boiling points and refractive indices indicated the presence of 2 methyl, 2.4 dimethyl and 2.4.6 trimethyl pyridines in different fractions.

Lanin and Pozhil'tsova (18) investigated the bases present in the tar from the carbonization of sapropel of the Karasine lake region of the Luga region, U.S.S.R. Primary and secondary amines were absent, but eleven pyridine homologues were isolated and identified. This work is of interest here as the sapropel may be considered as an oil shale in the process of formation.

The bases isolated from and identified in shale oils are listed in Table 1.

QUINOLINE BASES.

Several investigators have stated that quinoline homologues are present among the bases from shale oil (4, 10, 19, 20).

Gavin (19) loosely describes the bases from shale oil as pyridine and quinoline homologues, but McKee (2) says that " it is highly improbable that quinolines . . . and their hydroderivatives are present in more than very small amounts in (De Beque) shale oil ".

Kogermann (10) claimed that bases from Estonian shale oil belong to the pyridine and quinoline series, though he did not confirm this statement.

Cane (4) appears to be the first investigator to have claimed the isolation of a quinoline base from a shale oil. After purification of one fraction of the bases from Tasmanian shale oil the refractive index and specific gravity fell within the range of the trimethyl quinolines; but, however, a close examination of his paper throws very serious doubt on the validity of his claim to have identified the base as a quinoline derivative.

Cossettini (20) reports that pyridine and quinoline bases are manufactured for pharmaceutical use from the oil-bearing shale from the Rescutta mine at Mt. Salvotti. Unfortunately the original paper was not available but from the abstract it seems that it gives merely a general and brief description of the process and products which have not necessarily been specifically characterized.

TABLE 1.

Tar Bases from Shale Oil.

(The numbers refer to the appropriate references.)

Base.	Identified in Shale Oils.	Sapropel Tar.
Pyridine	5, 6, 7, 15	—
2 Methyl pyridine	1, 7, 12, 15, 17	—
3 ,, ,,	12, 13, 15	18
4 ,, ,,	12, 13	—
3 Ethyl pyridine	—	18
2 Butyl pyridine	—	18
2.3 Dimethyl pyridine	8, 12	—
2.4 ,, ,,	7, 12, 15, 17	18
2.5 ,, ,,	7, 13, 15	—
2.6 ,, ,,	7, 12, 15	18
3.4 ,, ,,	13	—
3.5 ,, ,,	13	—
2 Methyl 6 Ethyl pyridine	12	18
2 ,, 4 ,, ,,	13	18
2 ,, 5 ,, ,,	16	18
4 ,, 3 ,, ,,	—	18
2.4 Diethyl pyridine	—	18
2.3.5 Trimethyl pyridine	13	—
2.3.6 ,, ,,	12	—
2.4.5 ,, ,,	13	—
2.4.6. ,, ,,	2, 4, 7, 8, 11, 16, 17	18
2.6 Dimethyl 4 Ethyl pyridine	13	—
2.3.4.6 Tetramethyl ,,	13	—
Pyrindane (5.6 dihydro-pyrindene)	13	—
Quinoline	17	—
2 Methyl quinoline	17	—

In recent work at the Oil Shale Research and Development Laboratories of the U.S. Bureau of Mines (17) on the bases present in shale naphtha the ultraviolet absorption spectra, boiling points and refractive indices indicated the presence of quinoline and 2-methyl quinoline in different fractions. Since these bases have not been identified previously in shale oil this evidence cannot be taken as conclusive in the absence of chemical confirmation.

It would appear, therefore, that no quinoline bases have yet been identified beyond all reasonable doubt in shale oil, but this must not be taken to mean that they are not present.

ISOQUINOLINE BASES.

Robinson (21) and Robinson and Goodwin (22) examined the higher boiling bases from Scottish shale oil and reported that the bases belonged to the isoquinoline series. This classification was based entirely on the negative nature of the cyanine test which was quoted by a contemporary (23) as distinguishing between quinoline and isoquinoline bases. However, the cyanine test is valid only for 2 or 4 methyl quinolines and a negative test does not exclude quinoline itself. We can therefore say that these workers had no real evidence for classifying their bases as isoquinoline homologues.

As a point of interest it may be mentioned that the name " Tetracoline " which Robinson applied to his C_{12} base has been applied to 2.5.7 trimethyl quinoline (24), though this base does not appear to be listed in Beilstein.

Mckee (2) remarked that " it is highly improbable that . . . isoquinolines and their hydroderivatives are present in more than very small amounts in the fractions of De Beque (Colorado) shale oil which boil below 300° C."

It is obvious, therefore, that no isoquinoline bases have yet been identified in shale oil, but this must not be taken to mean that they may not be present.

OTHER BASES.

It has been observed by the author that the carefully purified bases from cracked shale gasoline still contain as much as 0·2% of sulphur. From the method of purification employed (25) there was no neutral oil left in the bases, so the sulphur must have been present in the molecular structure of the bases. Thiazole bears the same relationship to the pyridine as does thiophene to benzene (e.g. pyridine b.p. 115° C., thiazole b.p. 117° C.) and is very similar in properties. It is therefore possible that thiazoles may be present in the bases, their similarity to the pyridines being a contributing factor to their having been overlooked. The 0·2% sulphur in the bases could be accounted for by the presence of approximately 1% of thiazoles.

SUMMARY.

The only organic nitrogen compounds that have been isolated and identified in shale oil are pyridine and its simple methyl and ethyl derivatives. The only bicyclic base isolated in pyrindane in which the pyridine ring is fused to a cyclopentane ring. Quinoline and isoquinoline derivatives have been claimed but have not been identified with certainty.

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NITROGEN IN OIL SHALE AND SHALE OIL.

III. Nitrogenous Products from the Pyrolysis of Porphyrins and Proteins.

By Geo. E. Mapstone, M.Sc., A.A.C.I., M.Inst.Pet.

Manuscript received, April 29, 1948. Read, June 2, 1948.

Introduction.

In considering the possible forms of nitrogen compounds that may be present in shale oil the first step is to examine the primary decomposition products of the nitrogen compounds present in shale, and the second step is to examine the secondary reactions that can give rise to, modify, or destroy the bases.

In the first paper of this series (1) it was suggested that the nitrogenous constituents of shale kerogens are of porphyrinic and protein origin, and that the original chlorophyll and proteins have been modified by bacteriological action.

The pyrolylic decomposition of these two classes of compounds will be considered in turn and then the secondary reactions of the bases, etc., discussed in a later paper.

Pyrolysis of Porphyrins.

Apart from a few, controlled low temperature pyrolytic reactions in solution in connection with porphyrin syntheses, there appears to be no reference in the literature of the pyrolytic decomposition of porphyrins. The highest temperature that appears to have been used in porphyrin treatment was applied by Treibs (2). On slowly heating pheophytin in petroleum to 250°–320° C. he obtained phylloerythrin, and further heating to 360° C. gave desoxophyllerythroætioporphyrin.

Since the rate of thermal decomposition of kerogen is not appreciable below about 400° C., even higher temperatures than this must necessarily be used in retorting shale. Unfortunately no data is available on the stability of the porphyrin nucleus at such elevated temperatures, but the phthalocyanines, which have a similar structure, are stable.

An approximate calculation of the boiling point of dexosophylloerythroætioporphyrin using Nekrasov's formula for hydrocarbons (3) indicates that it would be well over 500° C. It is quite possible, however, that some of this porphyrin would distil, if sufficiently stable and thus appear in the crude shale oil.

Since the porphyrin molecule contains four substituted pyrrole nuclei it is a reasonable supposition that homologues of pyrrole will be among the products of thermal decomposition of porphyrins.

Pyrolysis of Proteins.

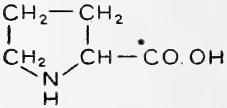
Ammonia is almost invariably present among the pyrolytic decomposition products of protein. It is also produced during the entire course of the pyrolysis of kerogen (4) though mainly at the higher temperatures (5). The condition by which the maximum yields of ammonia may be obtained from the shale have been the objects of many investigations (e.g. 5, 6, 7, 8, 9).

The greater proportion of the nitrogen in the kerogen always remains in combination in the residual coke from which it can be recovered in the form of ammonia by a current of steam (6, 8). Just as slow retorting of the shale increases the yield of ammonia at the expense of the residue, so does the use of high temperature increase the yield of ammonia at the expense of the nitrogenous constituents of the oil.

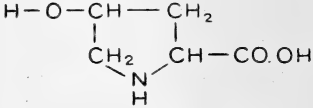
Of the amino acids occurring in proteins, proline (I) and hydroxyproline (II) both contain the hydrogenated pyrrole or pyrrolidine nucleus, and tryptophane (III) is a substituted indole (benzpyrrole).

The presence of indole among the pyrolytic decomposition products of proteins could be explained by the decomposition of tryptophane if present, while decarboxylation accompanied by dehydrogenation would convert proline and hydroxyproline into pyrrole. This, however, does not explain the origin of the pyrrole homologues in the shale oil, and these have been detected among the higher tar bases (4, 10), of which they may constitute the greater portion. Among the products of the pyrolysis of silk fibroin Johnson and Daschavsky (11, 12) identified quinoline and indole. They isolated indole from the acid and caustic washed oil. Since silk fibroin does not contain tryptophane, it could not have come from this source and was probably formed by the decomposition of the trimer of pyrrole as described in the next paper of this series.

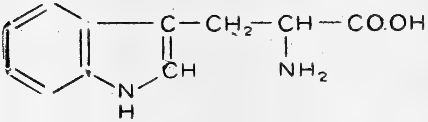
I. PROLINE.



II. HYDROXYPROLINE.



III. TRYPTOPHANE.



They suggested that the quinoline was formed by the pyrolysis of phenylalanine dipeptide residues which give rise to phenyl propionamide, which in turn was dehydrated, dehydrogenated and cyclized to quinoline. This purely theoretical mechanism for the reaction cannot be the full story, as the quinoline was formed by the decomposition of the alkali extract of the pyrolysis tar when attempts were made to purify it (12).

They also found that the acid extract of their oil possessed the odour of pyrrole. Pyrrole tests were always positive, but no treatment was found that enabled isolation of definite substances as they resinified rapidly in acid solution, and they oxidized and resinified on exposure to air.

Pictet and Cramer (12) distilled ovalbumin under reduced pressure and identified indole, several amides and a base which they tentatively considered to be a dihydroaniline, among the decomposition products.

Michelmann (14) observed that the pyrolysis of leather scrap gave an abundance of pyrocoll and pyrroles, and patented a process for the industrial preparation of pyrroles by the destructive distillation of collagenous materials such as glue, gelatine and leather scrap (15). Meir (16) also utilized leather scrap for the production of pyrroles.

Domingues de Campo (17) detected pyrrole in the smoke of leaves which did not contain nicotine. In the light of the evidence presented here it seems probable that the pyrrole was formed from the proteins in the leaf.

As early as 1858 Anderson (18) isolated pyrrole in a pure condition from the so-called bone oil or Dippel's oil which was obtained by the destructive distillation of bones. Thorpe (19) listed ammonia, fatty acids, nitriles, pyrrole, pyridine, quinoline and their homologues and some primary amines and amides among the products of the destructive distillation of bones. The formation of these various products is considered to be due to the following reactions: decomposition of the protein matter to give pyrrole and its homologues, and ammonia; the formation of nitriles and amides by the action of the ammonia on the fats and fatty acids; and the formation of pyridine and its derivatives by the condensation of ammonia with acrolein from the decomposition of the glycerides.

Troensgaard and Mygind (20) demonstrated the presence of a pyridine nucleus in proteins by hydrogenating acetylated gliandin and casein with sodium in pyridine-free amyl alcohol, hydrolysing in the cold and fractionating the bases obtained. They thus isolated 0·25% of piperidine. They suggested, however, that the piperidine was obtained by the hydrogenation of a piperidone rather than a pyridine grouping.

Troensgaard (21) hydrogenated proteins in water-free media and examined the basic fractions after partial hydrolysis. He found some diketo-piperazine rings had been hydrogenated to piperidine rings. Pyrrole rings were detected in some fractions, and piperidine was found in one hydrogenated protein.

No known naturally occurring amino acids from proteins contain a pyridine or piperidine nucleus, so pyridine homologues present in shale oil must have been produced by secondary reactions. However, cyclization of lysine (IV) or of arginine (V) would give rise to a piperidine nucleus. This same structure is present in the imide of glutamic acid (VI) but, in this case, pyridine alone would be obtained on decarboxylation and dehydrogenation.

IV. Lysine $HN_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH(NH_2)\text{–}CO_2H$.
V. Arginine $NH{=}C(NH_2)\text{–}NH\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH(NH_2)\text{–}CO_2H$.
VI. Glutamic acid $HO_2C\text{–}CH_2\text{–}CH_2\text{–}CH(NH_2)\text{–}CO_2H$.

It seems probable that the piperidine that Troensgaard obtained from the reduction of proteins was obtained by hydrogenation of the lactim of arginine after initial partial hydrolysis of the protein.

Carbonization of protein matter may, by promoting cyclization of these amino acids, give rise to pyridine, but not to its homologues. Only very small amounts of pyridine itself have been found among the bases in shale oil (22, 23, 24), so this mechanism does not seem to be of much importance even if it does occur.

Sibata and Sioya (25) found 7·3% by volume of pyridine type bases in the crude fuel oil obtained by the destructive distillation of sewage sludge. From the distillation range the basic oil was attributed to contain 34% quinoline, 18% collidine and about 5% pyridine. This observation of the formation of pyridine type bases is of interest because the nitrogenous constituents of the sewage sludge would be proteins which had been subjected to bacterial action, and would have had the opportunity to condense with aldehydes from the bacterial oxidation of carbohydrates, etc., to give heterocyclic nitrogen compounds as suggested by Maillard (26) in the formation of melanoids as an intermediate in coal formation.

Pictet and Chou (27) condensed casein with methylal in the presence of hydrochloric acid, dried the reaction product and distilled it with lime. They obtained a yellow oil which contained primary, secondary and tertiary bases, from which they isolated and identified pyridine, 2.6 dimethyl pyridine, isoquinoline and 4 methyl isoquinoline. Several other bases were isolated and characterized but not identified. They were unable to detect the slightest trace of quinoline in the oil. In a control experiment without the addition of methylal none of the pyridine type bases was formed.

Maillard (28) also observed that the amino acids from protein hydrolysis condensed with aldehydes to give pyridine bases.

Parker, Gutzeit, Bratton and Bailey (29) distilled cotton seed meal with a nitrogen-free lubricating oil, which acted also as a liquid medium for control of the low temperature pyrolysis. They obtained 337 lb. of crude bases from 23 tons of the meal. At least 50% of the bases were insoluble in petroleum ether and they averaged more than one nitrogen atom per molecule. Also, the bases exhibited an exceptional tendency to tar formation. Pyridine and the following thirteen other bases containing the pyridine nucleus were isolated and identified.

2, 3, and 4 Methyl Pyridines.
3 Ethyl Pyridine.
2,4; 2.6: and 3.5: Dimethyl Pyridines.
2.4.6. Trimethyl Pyridine.
Quinoline and Isoquinoline.
Quinolidine and Lepidine.
2.3.8. Trimethyl Quinoline.

Another base which appeared to be an alkylated dihydroquinazoline was isolated and characterized but not identified. Pyrazines and pyrimidines were suspected but a search for diazines was fruitless.

Boisselt and Louis (30) carbonized solvent-extracted grape seeds and " marc " from the wine industry, and obtained ammonia and pyridine bases in the distillate amounting to approximately 0·4% by weight of the charge.

DISCUSSION.

On the basis of the evidence presented in this review it appears that the nitrogen compounds that may be present in shale oil are extremely varied. Thus pyrrole homologues and possibly porphyrins and their intermediate decomposition products can be expected from the porphyrins present in the kerogen. Proteins and modified proteins could give rise to pyrrole and pyrrole derivatives such as indole and pyrocoll, as well as to pyridine type bases including quinoline and isoquinoline, and to diazines, amides and nitriles. Ammonia liberated from protein material, etc., is very reactive at the high temperature involved in the retorting process, so secondary reactions involving the formation of heterocyclic nitrogen compounds must not be overlooked. Also, secondary reactions involving the modification and decomposition of the nitrogen compounds formed during the initial pyrolysis of the kerogen no doubt have a very important bearing on the nature and distribution of the nitrogen compounds present in the resultant crude oil. These reactions will be dealt with in a subsequent paper.

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NITROGEN IN OIL SHALE AND SHALE OIL.

IV. PYROLYTIC REACTIONS INVOLVING THE FORMATION AND DECOMPOSITION OF TAR BASES.

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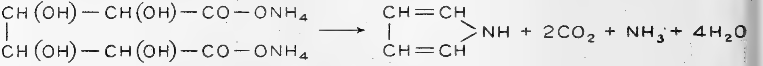
A study of the simple homologues of the bases present in the shale oil is a help in understanding the reactions occurring during the pyrolysis of the kerogen and the subsequent refining of the oil.

Pyridine and pyrrole homologues have been detected in shale oil and pyrolytic reactions involving their formation and decomposition will be discussed. Although none have yet been detected in shale oil, heterocyclic nitrogen compounds with two or more hetero-atoms in the molecule may be present and are therefore included in the review.

SYNTHESIS OF PYRROLES.

Pyrrole itself can be synthesized by distilling the ammonium salt of mucic or saccharic acid (1, 2).



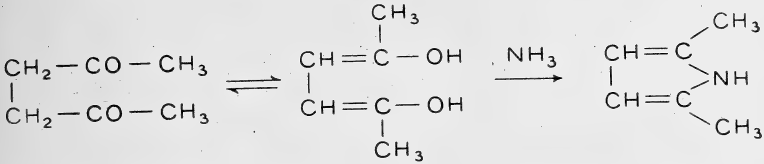
If monoalkylamines are used instead of ammonia in this synthesis N-alkyl pyrroles result (3, 4). On pyrolysis these readily rearrange to α alkyl pyrroles (5, 6, 7).

Pyrrole is also produced in small quantity by the action of heat on mixture of acetylene and ammonia (1, 8, 9, 10).

When butadiene and ammonia were passed over heated catalysts Schneider, Beck and Hausser (8) observed that the pyrrole ring was formed directly by ring closure without intermediate cleavage and with liberation of hydrogen, and that no materially greater amount of six, than of five membered ring compounds, were formed.

Pyrolysis of diethylamine gave rise to small yields of pyrrole (11, 12, 13) and N-ethyl aniline gave traces of indole (14) while N.N. dimethyl-o-toluidine gave relatively good yields of 1. methyl indole (15).

Since kerogen always contains an appreciable amount of oxygen, the presence of aldehydes and ketones in the crude shale oil is to be expected. γ di-ketones readily condense with ammonia to give pyrroles even in the cold (1, 16, 17, 18). This is the Paal-Knorr reaction, e.g.



Carbohydrate materials such as cellulose are reported to be among the pregenitors of coal (19) and, as coal and shale are often claimed to have a similar origin, it may be possible that such materials constitute part of the kerogen. Furanes are formed during the pyrolysis of carbohydrates and it is probable that, by reaction with the ammonia that is produced during the pyrolysis of kerogen, pyrroles would be formed.

Shmook (20) obtained a product which gave the characteristic pine splinter reaction of pyrroles by heating glucose, starch or pentosans with ammonium salts. Better yields were obtained under reducing conditions. He also obtained a distillate which gave characteristic pyrrole reactions by passing ammonia through a boiling glycerine solution of glucose.

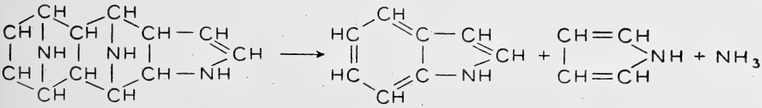
Wilson (21) passed ammonia and furan over activated alumina at 400° C. and identified pyrrole, pyrocoline, indole and carbazole in the products.

Yur'ev (22, 23) studied the reciprocal transformation of heterocyclic compounds with five-membered rings, and obtained yields of up to 40% of pyrrole by the treatment of furan with ammonia over an alumina catalyst at 550° C. The vapours of the product obtained by passing furfural and ammonia over alumina also gave an intense pine splinter reaction.

Granelli (24) obtained 2-methyl 3-ethyl pyrrole by passing 2.4 dimethyl pyridine and hydrogen over a nickel catalyst. However, this ring contraction does not seem to be likely to occur during shale carbonization.

PYROLYTIC REACTIONS OF PYRROLE WHICH RETAIN THE PYRROLE NUCLEUS.

Pyrroles polymerize extensively, particularly in the presence of acids, and the polymers do not depolymerize simply on heating but decompose to give a variety of products. The trimer of pyrrole is decomposed by heat to give pyrrole, ammonia and indole thus (1, 7, 25).



Similarly the dimer of ethyl pyrrole gives ammonia and diethyl indole on heating (7, 26).

Petrie (27) identified the deposit that formed in shale oil distillates on standing as a pyrrole polymer.

The crude secondary amines from shale oil are thermally unstable and decompose when distilled, even under vacuum, to give ammonia, free carbon and tertiary amines (28). It is logical to presume that the reaction involving the evolution of ammonia is similar to the decomposition of tripyrrole. The formation of tertiary bases is almost certainly due to ring enlargement by α-alkyl groups as discussed later.

Skatole or β-methyl indole is readily demethylated to indole by heating, a reaction which can be realized by heating small amounts of skatole in a test-tube over a free flame (7, 29).

Pictet and Rilliet (30) observed that pyrrole readily condenses with formalin to give an insoluble, hard, dark red substance. In the presence of acid they obtained an insoluble white product which gave α methyl pyrrole when distilled alone.

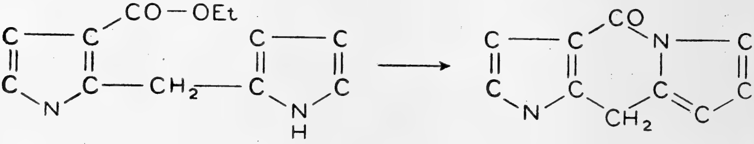
Backmann and Heisey (31) have isolated mono- and di- (amino-methyl) pyrroles from the tarry condensation products of pyrroles, secondary amines and formaldehyde. These products were unstable and decomposed on distillation.

Calvin *et al.* (32, 33) have identified α β γ δ tetraphenyl porphine and the corresponding chlorin as the main condensation products of benzaldehyde and pyrrole.

These aldehydic condensation products of pyrrole indicate a possible mechanism by which the molecular weight of some of the nitrogenous constituents of shale oil could be increased to give fractions of boiling point higher than the retorting temperature.

From certain dipyrrylmethanes Corwin and co-workers (34, 35) have synthesized a new class of heterocyclic base, the dipyrrolo-pyridones. They remark, " Compounds of this new class have aroused interest in the laboratory because their colour and fluorescence in organic solvents markedly resemble those of crude oil. Since decomposition products of chlorophyll might conceivably be responsible for the fluorescence in crude oils and might also be related to these synthetic products, the possibility exists that analogues of these synthetic products occur in nature."

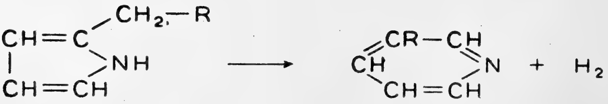
The new class of base is formed by the reaction :



Since chlorophyll degradation products are present in kerogen, it is quite conceivable that this class of base may be present in shale oil.

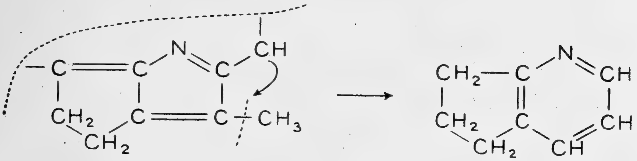
Conversion of Pyrroles to Pyridines.

One of the characteristic pyrogenic reactions of α substituted pyrroles is the enlarging of the five-membered ring to a six-membered ring (e.g. 1, 5, 7, 36, 37), thus :



where " R " can be almost any radicle. Substitution of the pyrrole nucleus does not appear to interfere with the reaction. For example, fair yields of quinoline were obtained by passing 2 methyl indole through a red hot tube (5, 37) and αα dipyridyl was formed as a by-product during the pyrolytic formation of 2 (α pyridyl) 5-methyl pyrrole (6). Oddo (38) has recently reviewed and discussed the mechanism of this reaction.

The presence of pyrindane in shale oil (39) could quite possibly be due to the fission of a desoxoporphyrin in the kerogen followed by ring enlargement by the α bridge carbon atom, thus:



Putochin (40) obtained 4-methyl pyridine by passing pyrrole and hydrogen over nickel at 200° C. This reaction is obviously complicated and the products were probably formed by the recombination of the decomposition products of the pyrrole.

Decomposition of the Pyrrole Nucleus.

Literature on pyrolytic reactions involving the decomposition of the pyrrole nucleus is extremely scanty.

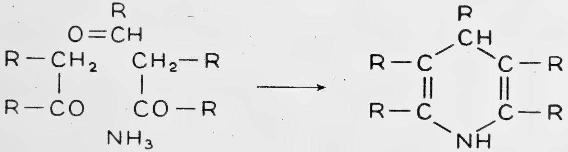
The formation and decomposition of tripyrrole, etc., as discussed earlier, does involve the decomposition of a pyrrole nucleus, but the formation of the indole is the main characteristic of the reaction.

Schneider, Beck and Hausser (8) observed that, on thermal catalytic decomposition pyrrole decomposed with the formation of hydrocarbons and they detected both hydrogen cyanide and ammonia among the products.

Woodward, Eisner and Haines (41) examined the pyrolytic decomposition products of nicotine. They obtained myosmine, nicotyrine, 2-methyl pyridine, 2-ethyl pyridine, 2-vinyl pyridine, pyridine, methylamine, ammonia and hydrogen cyanide among the products. These products indicated that the N-methyl pyrrolidine ring appears to be more susceptible to pyrogenic decomposition than the pyridine ring.

Synthesis of Pyridines.

The classical pyridine synthesis of Hantzsch (37) involves the condensation of aldehydes and/or ketones with ammonia to give a dihydro pyridine which is readily oxidized to the pyridine.



Since kerogen always contains an appreciable amount of oxygen, the presence of aldehydes and ketones in the crude oil is to be expected and a fair proportion of them will condense with ammonia during the pyrolysis of the kerogen and any subsequent distillation. Horne, Finley and Hopkins (28) found that aldehydes and ketones in crude shale oil could be accounted for after distillation only as tertiary amines.

From the condensation products of acetaldehyde and ammonia Tschitschibabin (43) isolated and identified α and γ picoline, β collidine, aldehyde collidine, α and β propyl pyridines and a small amount of α propenyl pyridine. Propionaldehyde and ammonia yielded 2- and 4-ethyl 3,5, dimethyl pyridines, while crotonaldehyde and ammonia gave 3-ethyl 4-methyl pyridine (44). β picoline may be obtained by the dry distillation of acrolein ammonia (45) or by the passage of acrolein and ammonia over aluminium phosphate at 350° C. (46).

Pyridine and pyridine derivatives are among the products of dry distillation of bones (1, 47). If the fat is removed from the bones prior to carbonization, no pyridine derivatives are formed, while free fatty acids are converted to their nitriles. The formation of pyridine bases in bone oil therefore depends on the presence of the glycerol which is dehydrated at high temperature to acrolein. This apparently condenses with ammonia formed from the protein matter to give the pyridine bases.

α picoline may be obtained by autoclaving ammonia, formalin and paraldehyde at 110° C. (48, 49) and the use of the other aldehydes and/or ketones gives corresponding complex mixtures.

Pictet and Stehlin (5) noted that ketones and amides can be condensed to pyridines by heat alone. Thus acetone and acetamide heated in a sealed tube at 250° C. gave a 2–3% yield of 2,4,6 trimethyl pyridine, while paraldehyde and acetamide gave a small yield of α picoline. Pyridine and other products were obtained by passing ethanol and ammonia over red hot iron (51). Similar results have been obtained with the higher alcohols and ammonia using zinc oxide catalyst at high temperatures (52). It has been suggested that aldehydes may be formed as intermediates (53).

Small yields of acetylene are obtained by the pyrolysis or partial combustion (54) of hydrocarbons. The high temperature condensation products of ammonia and acetylene have been studied rather extensively and pyridine derivatives have been isolated and identified among the products. Aldehyde ammonia appears to be an important intermediate in the condensation and has been isolated from the reaction mixture (8, 9, 55). Products isolated and identified from the ammonolysis of acetylene are listed in Table 1.

By condensation of methylamine and acetylene at 300° C. over zinc bromide-pumice catalyst Nicodemus and Schmidt obtained a product containing 25–30% pyridine and 50–60% of pyridine homologues (56).

In 1877 Ramsay (57) observed the formation of pyridine by the pyrolytic condensation of acetylene and hydrogen cyanide, a reaction which is analogous to the thermal polymerization of acetylene to benzene. Meyer and Wesche have (10) identified pyrrole, pyridine, quinoline and benzonitrile among the products of this reaction.

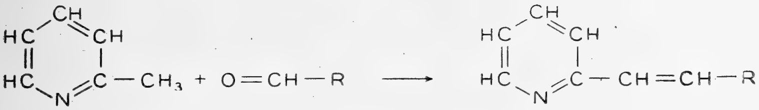
Tschitschibabin (13) has also obtained pyridine bases by the condensation of ammonia and ethylene over an alumina catalyst.

Small yields of pyridine bases have been obtained by heating ammonium bases or salts with glucose (58) or glycerol (59, 60, 61).

Kline and Turkevich (11) examined a number of possible pyrolytic syntheses of pyridine and obtained mixtures of pyridine and piperidine from ammonia and tetra-hydrofurfuryl alcohol, dihydropyran and pentamethylene oxide at temperatures in the vicinity of 400° C.

REACTIONS OF PYRIDINE WHICH RETAIN THE PYRIDINE NUCLEUS.

Pyridine bases which have a methylene group in the α or γ position show exceptional reactivity and condense readily with aldehydes. The mechanism of this reaction has recently been discussed by Roberts (62).



In this manner high boiling pyridine homologues would be formed from lower boiling materials.

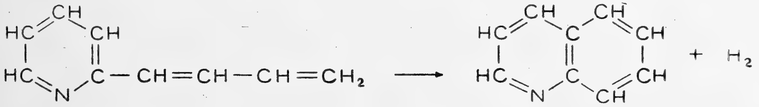
TABLE 1.

Products of the Condensation of Ammonia and Acetylene.

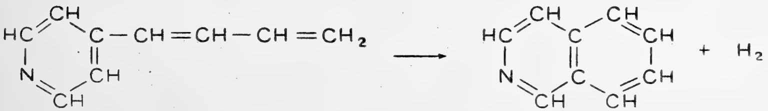
Products.	Reference.
Pyridine	10, 87
2 Picoline	9, 55, 88
3 Picoline	9, 55
4 Picoline	89, 90
1.4 Dimethyl pyridine	89, 90
2 Methyl 3 Ethyl pyridine	9
2 Methyl 5 Ethyl pyridine	9, 55
3 Methyl 4 Ethyl pyridine	55, 89, 90
2.3.6. Trimethyl pyridine	55
Indole	10
Pyrrole	1, 8, 9, 10
Quinoline	10
Aldehyde ammonia	8, 9, 55
Monoethylamine	55, 91, 92
Diethylamine	91, 92
Triethylamine	92
Aniline	10
Acetonitrile	9, 93
Benzonitrile	10

It must also be remembered that the nature of the side chains present in the high molecular weight bases will have an important bearing on the nature of the products of pyrolysis.

If the position adjacent to a long chain substituent is vacant it is conceivable that quinolines or isoquinolines could be formed by ring closure. Thus the condensation product of acrolein and α picoline could cyclise to quinoline.



Similarly γ picoline could give isoquinoline.



This suggests that benz-pyridines, which are yet to be identified for certainty in shale oil, could be derived from the simpler pyridines by secondary reactions.

On heating N-alkyl pyridinium compounds in a sealed tube to about 300° C. the alkyl group migrates to the α or γ position in the ring to give substituted pyridines (e.g. 1, 7, 63, 64, 65). This reaction is similar to the Hoffmann-Martius rearrangement, the mechanism of which is still in dispute, although recent evidence shows that the reaction involves the formation of free radicles. The voluminous literature now appearing on the mechanism of the cracking of hydrocarbons (e.g. 66, 67, 68) has shown beyond doubt that acceptance of radicle formation is necessary to explain the results. Shale carbonization involves the cracking of the kerogen to obtain the crude oil, so alkylation of pyridine homologues during the process may well take place.

If pyridine vapour is passed through a red hot tube dipyridyls are formed in a manner analogous to the formation of diphenyl from benzene. Of the six possible isomers the 44′ isomer is the only one that has not been identified in the condensation products which also contains some tripyridyls (1). Similarly α picoline gives dipicolyls, lutidines yield dilutidyls, collidines yield dicollidyls and quinoline yields diquinolyls (7). By extending this reaction it is possible to conceive the formation of very high molecular weight materials containing pyridine nuclei. Also, pyrolysis of nicotinic acid gives small yields of $\beta\beta'$ dipyridyl ketone (69).

DECOMPOSITION OF THE PYRIDINE NUCLEUS.

References in the literature to the pyrolytic decomposition of the pyridine nucleus are extremely few. This is no doubt due to the fact that, although the free energy of formation of pyridine from the elements is positive and increases with temperature (11) the simplest decomposition mechanism, involving the formation of vinyl acetylene and hydrogen cyanide, also has a high positive free energy (70).

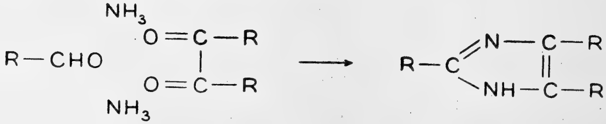
The author has observed hydrogen cyanide corrosion by the products from the cracking of crude shale oil, which contains pyridine homologues along with other nitrogen compounds (70).

On cracking the pyridine bases from brown coal tar Ruhemann (71) obtained from 6% to 7% by weight of hydrogen cyanide as well as some dipyridyls.

FIVE-MEMBERED RINGS WITH TWO NITROGEN ATOMS.

Pyrazoles are not very likely to be formed in the shale kerogen or during its pyrolytic decomposition as they are cyclic hydrazine derivatives. Pyrazole itself is stable to 300° C. but related compounds are less stable, thus N-phenyl-pyrazole melts with decomposition at 178° C. (7). The dihydropyrazoles or pyrazolines are unstable and decompose on heating to give cyclopropane derivatives (72).

The imidazoles or glyoxalines are formed by the condensation of ammonia and aldehydes with 1·2 diketones (72), thus:

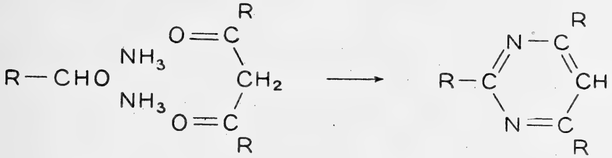


There is a scarcity of data available regarding the thermal stability of these compounds, but imidazole itself boils at 256° C. (74) and it is reported that the passage of N-methyl imidazole through a red hot tube causes rearrangement to C-methyl iminazole (7, 75).

SIX-MEMBERED RINGS WITH TWO NITROGEN ATOMS.

Pyridazines, like pyrazoles, are cyclic hydrazine derivatives and it is therefore most unlikely that this ring structure would be present in shale kerogen or formed during its pyrolytic decomposition. They will therefore not be discussed further.

Substituted pyrimidines may be obtained by the pyrolysis of proteins (76) or by the condensation of ammonia and an aldehyde with β diketones, thus :



The condensation of acetone and ammonia in the presence of ammonium salts yields 2.2.4.6.6. pentamethyl 1.2.5.6. tetrahydro pyrimidine (77). It was suggested that pyrolysis of this compound would split off methane from the gem dimethyl groups to give the trimethyl pyrimidine. Uracil or dihydroxy pyrimidine is an essential constituent of some nucleic acids as are some substituted purines which contain the pyrimidine and imidazole rings fused together. It is therefore possible that small amounts of these structures may be present in shale kerogen or its decomposition products. Uric acid, which is trihydroxy purine gives urea, hydrogen cyanide, cyanuric acid and carbon on dry distillation (78, 79).

Pyrazines occur in the fermentation products of sugar. Thus αγ dimethyl and trimethyl pyrazines have been isolated from fusel oil (61). The chief constituent of the bases produced by the action of ammonia on glucose is methyl pyrazine (61), pyrazine and dimethyl pyrazines being formed at the same time. αγ dimethyl pyrazine is formed together with pyridine bases and other alkyl pyrazines, e.g. α methyl γδ diethyl pyrazine, upon distilling glycerol with ammonium salts (61).

Pyrazines are also formed by the condensation of two molecules of α amino-aldehydes or ketones, the intermediate dihydro pyrazine being readily oxidized to the pyrazine by atmospheric oxygen (80).

The pyrazine nucleus appears to be reasonably heat stable as tetraphenyl pyrazine, which melts at 246° C., sublimes without decomposition (74).

RINGS CONTAINING NITROGEN AND ANOTHER HETERO ATOM.

By condensing acetylene with ammonia and hydrogen sulphide or sulphur Nicodemus (81) obtained a product which consisted largely of thiophene together with alkyl thiophenes, mercaptans, pyridine homologues and some materials which contained both nitrogen and sulphur. The structure of these latter materials was not determined but they were partly thiocyanate and partly basic in character. Since diketotetrahydrothiazole is obtained by the evaporation of thiocyanoacetic acid with acids (82) it appears likely that the basic portion of these nitrogen and sulphur containing materials are thiazoles.

It is possible that oxazoles could be formed in an analogous manner, but the principal effect of adding steam instead of hydrogen sulphide to the reactants was to greatly increase the yield of pyridine bases (83). Pyrroles are more stable than the furans but less stable than the thiophenes (84). Since oxazoles and thiazoles have the same relationship to one another as have furans and thiophenes, it appears that, although thiazoles may be obtained, the formation of oxazoles is much less certain.

Also, isoxazoles and the corresponding isothiazoles are not considered as likely to be present in the shale kerogen or shale oil as they are substituted hydroxylamines.

The six-membered ring compounds containing nitrogen and another heterocyclic atom are much less well known than their five-membered ring analogues with perhaps the exception of phenthiazine and phenoxazine. The former is, normally prepared by heating diphenylamine with sulphur, but no pyrolytic preparation of the latter appears to have been used.

The two fused benzene rings can be expected to stabilize the structure of the heterocyclic ring, but phenthiazine boils with decomposition at 371° C. (74). In view of the relatively greater thermal stability of the five-membered than the six-membered ring structure containing an oxygen or sulphur atom it seems likely that the most probable representatives of this group to be found in shale oil are the thiazoles.

COMPOUNDS WITH MORE THAN TWO HETERO ATOMS.

It is considered that the only compounds containing more than two hetero atoms in the ring that warrant consideration in this discussion are cyanuric acid and its derivatives. On destructive distillation cyanuric acid (m.p. 360° C. (74)) and its esters decompose to cyanic acid (85).

Kirner (85) lists cyanuric acid among the nitrogenous products isolated from soil humus, humic acid preparations and peat, so it may also be present in shale kerogen in small amounts. Destructive distillation of cyanuric acid or its esters (86) yields cyanic acid, which can repolymerize to give some cyanuric acid in the distillate. In this manner both cyanic and cyanuric acid may be present in small amounts in shale oil.

SUMMARY.

From this review of the secondary pyrolytic reactions that could take place during the retorting of oil shale it is apparent that a wide range of cyclic nitrogen compounds may be present in shale oil. These include pyrrole and pyridine, their homologues and benz-derivatives, together with materials which contain more than one heterocyclic ring. Diheterocyclic compounds also may be formed though, for stability, the two hetero atoms should not be adjacent. It is also possible that non-cyclic, non-basic nitrogenous compounds such as nitriles and thiocyanates may be present.

Decomposition of the bases formed may influence the products appreciably, thus pyrroles can give rise to indoles and ammonia while pyridines would tend to give mainly dipyridyls with a small amount of nuclear decomposition to give hydrocarbons and hydrogen cyanide.

ACKNOWLEDGEMENT.

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ELECTRO-MAGNETO-IONIC OPTICS.

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1. Introduction.

The study of electric waves emitted under certain conditions by discharge tubes, by the Ionosphere and the Solar Atmosphere, has not hitherto been accompanied by a theory, based on Maxwell's equations, which takes account of the effects which may be due to static electric fields.

It is proposed here to give the fundamental set of equations from which such a theory may be developed. The main restriction involved in this set is that the motion of the positive ions is neglected.[1]

The essential problem to be considered is to determine the electric waves which can exist in a medium consisting of electrons (N_0 per cc.), positive ions (N_i per cc.) and molecules (or atoms) and subject to static electric and magnetic fields ($\mathbf{E}_0$ and $\mathbf{H}_0$ respectively).

A preliminary note on this work has been published[2] in *Nature.*

2. Notation.[3]

The principal notation to be used is given in the following table, where the static values of the variables are indicated by means of a subscript o.

e, m =electron charge and mass respectively, in e.s.u.
N, N_i =electron and positive ion densities respectively.
$\mathbf{U}$ =mean velocity of the electrons.
$\mathbf{E}$, $\mathbf{H}$ =electric vector (e.s.u.) and magnetic vector (e.m.u.) respectively.
$\mathbf{A}$, V =vector and scalar potentials respectively.
ω, ν =wave angular frequency and electron collision frequency respectively.
q^{-1}, λ =wave-velocity and wave-length respectively.
r, ζ defined by: $r=1-q\,U_1$, $\zeta=c^2q^2-1$, where U_1 is the x-component of $\mathbf{U}_0$ the drift-velocity.
p_0 $=\sqrt{4\pi N_0e^2/m}=5\cdot65\times10^4\sqrt{N_0}$.
Ω_0 $=(-e/mc)\,\mathbf{H}_0=$the gyro-frequency vector.
T =mean kinetic energy of an electron.
p =partial pressure of the electrons $=\frac{2}{3}N\,T$.
τ $=2T/3m$.
$\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ =orthogonal unit vectors, parallel to the x, y and z axes respectively.

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[1] This restriction will be removed in a later publication.

[2] *Nature*, 161, April 17, 1948.

[3] All Clarendon type and the symbol $\breve{\Omega}_0$ indicate vectors.

$\breve{\nabla} \quad =\mathbf{i}\,\dfrac{\partial}{\partial x}+\mathbf{j}\,\dfrac{\partial}{\partial y}+\mathbf{k}\,\dfrac{\partial}{\partial z}.$

$D_{\mathrm{t}} \quad =\dfrac{\partial}{\partial t}.$

$\Box^2 \quad =\nabla^2-c^{-2}\,D_{\mathrm{t}}^2.$

$D \quad =\dfrac{\partial}{\partial t}+(\mathbf{U}\,\breve{\nabla}). \qquad D_0=\dfrac{\partial}{\partial t}+(\mathbf{U}_0\breve{\nabla}).$

c =velocity of light in vacuo.

The components of any vector $\mathbf{U}_0$ or $\mathbf{u}$ are denoted by U_1, U_2, U_3 or u_1 u_2, u_3 and the components transverse to the x-axis are denoted by $\mathbf{U}_{\mathrm{T}}$ or $\mathbf{u}_{\mathrm{T}}$.

3. THE FUNDAMENTAL EQUATIONS.

The fundamental relations between the six variables N, $\mathbf{U}$, $\mathbf{E}$, $\mathbf{H}$, $\mathbf{A}$, V are as follows (when the motion of the positive ions is neglected).

$$D_{\mathrm{t}}V=-c\breve{\nabla}\,\mathbf{A}, \quad \ldots\ldots \quad (1)$$

$$\mathbf{E}=-c^{-1}D_{\mathrm{t}}\mathbf{A}-\breve{\nabla}\,V, \quad \ldots\ldots \quad (2)$$

$$\mathbf{H}=\breve{\nabla}\times\mathbf{A}, \quad \ldots\ldots \quad (3)$$

$$4\pi ec^{-1}N\mathbf{U}=-\Box^2\mathbf{A}, \quad \ldots\ldots \quad (4)$$

$$4\pi e(N-N\mathrm{i})=-\Box^2 V, \quad \ldots\ldots \quad (5)$$

$$D\mathbf{U}+\nu\mathbf{U}=(e/m)(\mathbf{E}+c^{-1}\mathbf{U}\times\mathbf{H})-N^{-1}\breve{\nabla}\tau N \quad \ldots\ldots \quad (6)$$

The relation (6) is derivable from Maxwell's theory of transport of momentum.[1]

It can also be derived in the following simple way.

A group of N electrons with a mean momentum $Nm\mathbf{U}$ will lose this momentum at the rate $\nu(Nm\mathbf{U})$ where ν is a constant which depends on the total number of other particles present per cc.; ν will be called the average collision frequency of an electron.

If $\mathbf{F}$ is the intensity of the electromagnetic force on an electron, i.e.

$$\mathbf{F}=\mathbf{E}+c^{-1}\mathbf{U}\times\mathbf{H},$$

and p is the partial pressure of the electrons, therefore

$$mN\frac{d\mathbf{U}}{dt}=Ne\mathbf{F}-\mathrm{grad}\;p-\nu Nm\mathbf{U}. \quad \ldots\ldots \quad (7)$$

Since $p=\tau mN$, (7) reduces to (6).

It is shown in the Appendix that (6) is consistent with the classical formulae of J. S. Townsend for the steady motions of electrons under the action of uniform static electric and magnetic fields.

From (1) to (6) we obtain the following relations between the static quantities N_0, $\mathbf{U}_0$, $\mathbf{E}_0$, $\mathbf{H}_0$, $\mathbf{A}_0$, V_0.

$$0=-c\breve{\nabla}\,\mathbf{A}_0, \quad \ldots\ldots \quad (1.0)$$

$$\mathbf{E}_0=-\breve{\nabla}\,V_0, \quad \ldots\ldots \quad (2.0)$$

$$\mathbf{H}_0=\breve{\nabla}\times\mathbf{A}_0, \quad \ldots\ldots \quad (3.0)$$

$$4\pi ec^{-1}N_0\mathbf{U}_0=-\Box^2\mathbf{A}_0; \quad \ldots\ldots \quad (4.0)$$

$$4\pi e(N_0-N\mathrm{i})=-\Box^2 V_0, \quad \ldots\ldots \quad (5.0)$$

$$D_0\mathbf{U}_0+\nu\mathbf{U}_0=(e/m)(\mathbf{E}_0+c^{-1}\mathbf{U}_0\times\mathbf{H}_0)-N_0{}^{-1}\breve{\nabla}\tau N_0 \quad \ldots\ldots \quad (6.0)$$

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[1] J. C. Maxwell, "Scientific Papers", Vol. 2, pp. 51-58. (Camb. Univ. Press, 1890.)

We now set

$$\left.\begin{array}{ll} N=N_0+n, & \mathbf{U}=\mathbf{U}_0+\mathbf{u}, \\ \mathbf{E}=\mathbf{E}_0+\mathbf{e}, & \mathbf{H}=\mathbf{H}_0+\mathbf{h}, \\ \mathbf{A}=\mathbf{A}_0+\mathbf{a}, & V=V_0+v, \end{array}\right\} \qquad (8)$$

and for a first approximation take n, **u**, **e**, **h**, **a**, v as relatively small periodic quantities of a common frequency.

On subtracting (1.0) from (1), (2.0) from (2), etc., using (8) and retaining only terms linear in n, **u**, **e**, etc., the following system of differential equations is obtained for a medium which is uniform when in the static state :

$$D_t v=-c\breve{\nabla}\mathbf{a}, \qquad (1.1)$$

$$\mathbf{e}=-c^{-1}D_t\mathbf{a}-\breve{\nabla}v, \qquad (2.1)$$

$$\mathbf{h}=\breve{\nabla}\times\mathbf{a}, \qquad (3.1)$$

$$N_0\mathbf{u}+\mathbf{U}_0 n=-(c/4\pi e)\square^2\mathbf{a}, \qquad (4.1)$$

$$n=-(1/4\pi e)\square^2 v, \qquad (5.1)$$

$$D_0\mathbf{u}+\nu\mathbf{u}=(e/m)\mathbf{e}+\breve{\Omega}_0\times\mathbf{u}+(e/mc)\mathbf{U}_0\times\mathbf{h}-\tau\breve{\nabla}(n/N_0) \qquad (6.1)$$

When the medium in the static state is not uniform (6.1) must be supplemented by additional terms.

On eliminating **e**, **h**, **u** and n between these equations we are left with (1.1) and the following equation in **a** and v :

$$(D_0+\nu-\breve{\Omega}_0\times)[-\mathbf{U}_0\square^2 v+c\square^2\mathbf{a}]=-p_0^2\mathbf{f}-\tau\breve{\nabla}\square^2 v \qquad (9)$$

where

$$\mathbf{f}=-c^{-1}D_t\mathbf{a}-\breve{\nabla}v+c^{-1}\mathbf{U}_0\times(\breve{\nabla}\times\mathbf{a}) \qquad (10)$$

(1.1) and (9) can be solved for **a** and v.

4. EQUATIONS FOR PLANE WAVES.

The solutions for plane waves propagated along the x-axis of rectangular coordinates are found by taking all the variables as proportional to

$$e^{i\omega(t-qx)}$$

where in general ω and q may be complex numbers.

The corresponding physical quantities will be taken as the real parts of the variables.

We may here now set

$$\left.\begin{array}{ll} D_t=i\omega, & D_0=i\omega r, \\ \breve{\nabla}=-i\omega q\mathbf{i}, & \square^2=-\omega^2c^{-2}\zeta, \end{array}\right\} \qquad (11)$$

where

$$r=1-qU_1, \qquad \zeta=c^2q^2-1. \qquad (12)$$

Then (1.1) becomes

$$v=cqa_1, \qquad (13)$$

and so from (9) we obtain

$$(\delta-\breve{\Omega}_0\times)(r\mathbf{a}_1+\mathbf{a}_\mathrm{T}-q\mathbf{U}_\mathrm{T}a_1)$$
$$=i\omega_0\{\mathbf{a}_1-\zeta^{-1}r\mathbf{a}_\mathrm{T}-\zeta^{-1}q\mathbf{U}_\mathrm{T}\times(\mathbf{i}\times\mathbf{a}_\mathrm{T})\}+i\tau\omega q^2\mathbf{a}_1, \qquad (14)$$

where

$$\delta=\nu+i\omega r, \qquad (15)$$

$$\omega_0=p_0^2\omega^{-1}. \qquad (16)$$

As a check we find that when $\mathbf{U}_0=0$ and $\tau=0$ (14) reduces to

$$(\nu+i\omega+i\omega_0\zeta^{-1})\mathbf{a}-i\omega_0(1+\zeta^{-1})\mathbf{a}_1-\breve{\Omega}_0\times\mathbf{a}=0$$

which agrees, as it should, with equation (13) in a previous publication.[1]

5. Solutions of the Equations for Plane Waves.

On setting in (14)

$$\begin{aligned}\mathbf{a}&=a_1\mathbf{i}+a_2\mathbf{j}+a_3\mathbf{k},\\ \mathbf{U}_0&=U_1\mathbf{i}+U_2\mathbf{j}+U_3\mathbf{k},\\ \breve{\Omega}_0&=\Omega_1\mathbf{i}+\Omega_2\mathbf{j}+\Omega_3\mathbf{k},\end{aligned}$$

and equating coefficients of **i**, **j** and **k** on both sides we obtain the following system of simultaneous equations in a_1, a_2, a_3.

$$\left.\begin{aligned}\alpha_1a_1+\alpha_2a_2+\alpha_3a_3&=0,\\ \beta_1a_1+\beta_2a_2+\beta_3a_3&=0,\\ \gamma_1a_1+\gamma_2a_2+\gamma_3a_3&=0,\end{aligned}\right\}\quad\ldots\ldots\ldots\ldots\ldots\ldots\quad(17)$$

where

$$\left.\begin{array}{lll}\alpha_1=\nu+i\psi-qb_1, & \alpha_2=\Omega_3+igU_2, & \alpha_3=-\Omega_2+igU_3,\\ \beta_1=-\Omega_3-qb_2, & \beta_2=\xi, & \beta_3=\Omega_1,\\ \gamma_1=\Omega_2-qb_3, & \gamma_2=-\Omega_1, & \gamma_3=\xi\end{array}\right\}\quad\ldots\ldots\quad(18)$$

$$\left.\begin{aligned}\psi&=\omega r-\omega_0-\tau\omega q^2,\\ \xi&=\nu+ir(\omega+\omega_0\zeta^{-1}),\end{aligned}\right\}\quad\ldots\ldots\ldots\ldots\ldots\ldots\quad(19)$$

$$\left.\begin{aligned}b_1&=\delta U_1+\Omega_3U_2-\Omega_2U_3,\\ b_2&=\delta U_2+\Omega_1U_3-\Omega_3U_1,\\ b_3&=\delta U_3+\Omega_2U_1-\Omega_1U_2,\end{aligned}\right\}\quad\ldots\ldots\ldots\ldots\ldots\quad(20)$$

$$g=\omega_0q\zeta^{-1}.\quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\quad(21)$$

If

$$\triangle=\begin{vmatrix}\alpha_1 & \alpha_2 & \alpha_3\\ \beta_1 & \beta_2 & \beta_3\\ \gamma_1 & \gamma_2 & \gamma_3\end{vmatrix}\quad\ldots\ldots\ldots\ldots\ldots\ldots\quad(22)$$

and α', α'', α''' are the cofactors of α_1, α_2, α_3 respectively, then the necessary and sufficient condition for (17) to have a finite solution is that

$$\triangle=0,\quad\ldots\ldots\ldots\ldots\ldots\ldots\quad(23.1)$$

and the solution is then given by

$$a_1=C\alpha',\ a_2=C\alpha'',\ a_3=C\alpha''',$$

i.e. by

$$\left.\begin{aligned}a_1&=C(\xi^2+\Omega_1^2),\\ a_2&=C[\xi(\Omega_3+qb_2)+\Omega_1(\Omega_2-qb_3)],\\ a_3&=C[\xi(-\Omega_2+qb_3)+\Omega_1(\Omega_3+qb_2)].\end{aligned}\right\}\quad\ldots\ldots\ldots\quad(24.1)$$

From this we have

$$a_{\mathrm{T}}=\sqrt{a_2^2+a_3^2}=C\sqrt{(\xi^2+\Omega_1^2)T}$$

where

$$T=(\Omega_3+qb_2)^2+(\Omega_2-qb_3)^2.$$

On expanding T and using (20) we obtain eventually

$$T=\Omega_{\mathrm{T}}^2r^2+2\Omega_{\mathrm{T}}U_{\mathrm{T}}qr(\delta\sin\theta+\Omega_1\cos\theta)+U_{\mathrm{T}}^2q^2(\delta^2+\Omega_1^2),$$

where θ is the angle between $\mathbf{H}_{\mathrm{T}}$ and $\mathbf{U}_{\mathrm{T}}$.

---

[1] V. A. Bailey, *Phil. Mag.*, 23, p. 929 (1937).

Accordingly from (24.1) we obtain

$$\left.\begin{array}{l} a_1 = C\chi\sqrt{\xi^2+\Omega_1^2},\ a_2 = a_{\mathrm{T}}\cos\varphi,\ a_3 = a_{\mathrm{T}}\sin\varphi \\ \text{where} \\ a_{\mathrm{T}} = C\chi\sqrt{r^2\Omega_{\mathrm{T}}^2 + 2arq\Omega_{\mathrm{T}}U_{\mathrm{T}} + bq^2U_{\mathrm{T}}^2}, \\ a = \delta\sin\theta + \Omega_1\cos\theta, \\ b = \delta^2 + \Omega_1^2, \end{array}\right\} \quad \ldots\ldots \quad (24.2)$$

C is an arbitrary constant, φ is the "angle" between $\mathbf{a}_{\mathrm{T}}$ and the y-axis and $\chi = e^{i\omega(t-qx)}$.

From (18) we have

$$\left.\begin{array}{l} \alpha_1 = \rho_1 + i\rho_2, \\ \beta_1 = \sigma_1 + i\sigma_2, \\ \gamma_1 = \tau_1 + i\tau_2, \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (25)$$

where

$$\left.\begin{array}{ll} \rho_1 = \nu r - q(\Omega_3U_2 - \Omega_2U_3), & \rho_2 = \omega r^2 - \omega_0 - \tau\omega q^2, \\ \sigma_1 = -\Omega_3 r - q(\nu U_2 + \Omega_1U_3), & \sigma_2 = -\omega rqU_2, \\ \tau_1 = \Omega_2 r - q(\nu U_3 - \Omega_1U_2), & \tau_2 = -\omega rqU_3. \end{array}\right\} \quad \ldots\ldots \quad (26)$$

On adding to the first column of $\triangle$, qU_2 times the second column and qU_3 times the third column we obtain

$$\triangle = \begin{vmatrix} \alpha & \alpha_2 & \alpha_3 \\ \beta & \beta_2 & \beta_3 \\ \gamma & \gamma_2 & \gamma_3 \end{vmatrix} \times r \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (27)$$

where

$$\begin{aligned} \alpha r &= \alpha_1 + \alpha_2 qU_2 + \alpha_3 qU_3, \\ \beta r &= \beta_1 + \beta_2 qU_2 + \beta_3 qU_3, \\ \gamma r &= \gamma_1 + \gamma_2 qU_2 + \gamma_3 qU_3. \end{aligned}$$

On using (18), (25) and (26) we find that

$$\left.\begin{array}{l} \alpha = \nu + i(\omega r - p_0^2\omega^{-1}r^{-1}s - \tau\omega q^2 r^{-1}), \\ \beta = -\Omega_3 + igU_2, \\ \gamma = \Omega_2 + igU_3, \end{array}\right\} \quad \ldots\ldots\ldots\ldots \quad (28)$$

where

$$s = 1 - \zeta^{-1}q^2U_{\mathrm{T}}^2. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (29)$$

From (27) and (28) we now obtain

$$\triangle = \alpha(\xi^2 + \Omega_1^2)r + \xi(\Omega_{\mathrm{T}}^2 + g^2U_{\mathrm{T}}^2)r + 2ig\Omega_1(\Omega_2U_2 + \Omega_3U_3)r \quad \ldots \quad (27.1)$$

where

$$\xi = \nu + i(\omega r + p_0^2\omega^{-1}\zeta^{-1}r). \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (30)$$

Hence the condition (23.1) becomes

$$r\alpha(\xi^2 + \Omega_1^2) + r\xi(\Omega_{\mathrm{T}}^2 + g^2U_{\mathrm{T}}^2) + irgU_{\mathrm{T}}S = 0 \quad \ldots\ldots\ldots\ldots \quad (23.2)$$

where

$$\left.\begin{array}{l} S = 2\Omega_1\Omega_{\mathrm{T}}\cos\theta, \\ \theta = \text{angle between } \mathbf{H}_{\mathrm{T}} \text{ and } \mathbf{U}_{\mathrm{T}}. \end{array}\right\} \quad \ldots\ldots\ldots\ldots \quad (31)$$

On multiplying (23.2) throughout by $i\omega^3\zeta^2$ it becomes

$$\begin{aligned} &[\omega^2(r^2 - \tau q^2) - p_0^2 + p_0^2\zeta^{-1}q^2U_{\mathrm{T}}^2 - i\omega r\nu]\,[(\omega^2\zeta r + p_0^2 r - i\omega\nu\zeta)^2 - \Omega_1^2\omega^2\zeta^2] \\ &\qquad - (\omega^2r^2 + p_0^2r^2\zeta^{-1} - i\omega r\nu)(\Omega_{\mathrm{T}}^2\omega^2\zeta^2 + p_0^4q^2U_{\mathrm{T}}^2) \\ &\qquad - p_0^2\omega^2 r\zeta qU_{\mathrm{T}}S = 0. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (23.3) \end{aligned}$$

The terms in (23.3) which contain ζ^{-1} mutually cancel. Hence (23.3) contains only positive powers of ω and ζ. It is of the 6th degree in ω and of the 8th degree in q.

On dividing throughout by p_0^6 and setting

$$\frac{\omega}{p_0}=w,\ \frac{\Omega_1}{p_0}=W_1,\ \frac{\Omega_T}{p_0}=W_T,\ \frac{\Omega_0}{p_0}=W_0,\ \frac{\nu}{p_0}=\rho \quad \dots\dots\dots\dots \quad (32)$$

(23.3) becomes

$$\begin{aligned}&[w^2(r^2-\tau q^2)-1+\zeta^{-1}q^2U_T^2-iwr\rho]\ [(w^2\zeta r+r-iw\rho\zeta)^2-W_1^2w^2\zeta^2]\\ &\qquad -(w^2r^2+r^2\zeta^{-1}-iwr\rho)(W_T^2w^2\zeta^2+q^2U_T^2)\\ &\qquad -w^2r\zeta qU_TS_0=0, \quad \dots\dots\dots\dots \quad (23.4)\end{aligned}$$

where

$$S_0=2W_1W_T\cos\theta \quad \dots\dots\dots\dots \quad (33)$$

In accordance with the Theory of Relativity we must always have

$$U_1<c,\ U_T^2<c^2-U_1^2 \quad \dots\dots\dots\dots \quad (34)$$

The equation of condition (23.3) (or its equivalent (23.4)) has at the least three physical aspects, namely :

I. It specifies the possible frequencies and coefficients of damping (or of secular growth) of waves which traverse the medium with a given (real) phase-velocity q^{-1}.

II. It specifies the possible refractive indices and coefficients of attenuation (or of spatial growth) under which waves of a given (real) frequency ω are propagated in the medium, i.e. it specifies the optical dispersion of the medium.

III. It specifies the possible frequencies and coefficients of damping (or of secular growth) of waves which can exist in the medium with a given (real) wave-length λ.

The general discussion of each of these aspects is very complicated ; for example Aspects II and III require, in general, the study of equations of the eighth degree.

Nevertheless it has been found possible to derive from (23.4) a number of interesting physical conclusions when the collision frequency ν is taken to be so small that ρ^2 is negligible.

When that is the case (23.4) reduces to the form

$$f(w,q)\equiv P(w^2,q)+i\rho rwQ(w^2,q)=0 \quad \dots\dots\dots\dots \quad (23.5)$$

where $P(w^2,q)$ and $Q(w^2,q)$ are certain polynomials.

When the equation

$$P(w^2,q)=0 \quad \dots\dots\dots\dots \quad (35)$$

is satisfied by a pair of values of w and q which are both real the corresponding wave will be called one of the First Species.

When (35) is satisfied by a pair of values of w and q such that at least one is complex the corresponding wave will be called one of the Second Species.

It has been found that under certain conditions a wave-group, composed of waves of the Second Species with frequencies in a narrow band about the frequency ω, can grow in amplitude as it progresses.*

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* When the motion of the positive ions is also taken into account it is found that besides these growing wave-groups we can now find waves of a given length which everywhere *grow with the lapse of time.*

This deduction from the theory suggests one explanation of the origin of stellar, solar and ionospheric noise.

The details of this work and other consequences of the present theory will be published in due course.

APPENDIX.

In the steady state when $d\mathbf{U}/dt=O$ (6) reduces to

$$\nu\mathbf{U}-\breve{\Omega}_0\times\mathbf{U}=\mathbf{R} \quad \text{..........................} \quad (36)$$

where

$$\mathbf{R}=-\sigma\mathbf{E}_0-N^{-1}\text{ grad }\tau N, \quad \text{................} \quad (37)$$

and $\sigma=-e/m$.

From (36) we obtain

$$\mathbf{U}=P\mathbf{R} \quad \text{................................} \quad (38)$$

where P is the operator

$$P=(\nu^2+\Omega_0^2)^{-1}[\nu\,..+(\breve{\Omega}_0\times\,..)+\nu^{-1}\breve{\Omega}_0(\breve{\Omega}_0\,..)] \quad \text{....} \quad (39)$$

When grad $N=0$ and $\mathbf{E}_0$ and $\mathbf{H}_0$ are uniform $\mathbf{U}$ becomes the drift velocity $\mathbf{U}_0$ and (38) then yields

$$\mathbf{U}_0=P(-\sigma\mathbf{E}_0). \quad \text{............................} \quad (40)$$

From (38) and (40) we obtain

$$N\mathbf{U}=N\mathbf{U}_0-P\tau\text{ grad }N. \quad \text{.....................} \quad (41)$$

The last term in (41) represents the diffusion of the electrons. On comparing it with (40) we deduce the following results:

The coefficients of diffusion along and transverse to the magnetic field $\mathbf{H}_0$ are proportional to the corresponding components of the drift velocity due to an electric force parallel to grad N.

This is equivalent to the results given by Townsend in Sections 91 and 92 of his book "Electricity in Gases" (Clarendon Press, 1915).

Townsend's formulae for the components of $\mathbf{U}_0$ along and transverse to $\mathbf{H}_0$ are also easily deduced from (40).

ASPECTS OF THE DIELS–ALDER REACTION.

PART III. A NOTE ON THE REPORTED REACTION WITH ANTHRAQUINONE.

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There appears to be little doubt that the Diels-Alder reaction does not take place with aromatic rings having a high degree of " aromatic character " except in the special cases where a double bond is conjugated with the ring. The polycyclic aromatic hydrocarbons which undergo the reaction—sometimes with unfavourable equilibria—contain either activated *meso* positions as in anthracene or a relatively fixed and sterically favourable system of double bonds as in perylene. The simple aromatics which react normally are limited to a few highly substituted thiophenes and furan and its derivatives, in which case again the reaction is markedly reversible.

On this view it seemed advisable to investigate a statement by Norton (1942) in a review of the Diels-Alder reaction that a benzene ring of 9, 10-anthraquinone can act as a diene in the reaction and can undergo 1, 4-addition of maleic anhydride. Such a reaction seems unlikely, particularly in view of the similar electron-deficient nature of the benzene rings of anthraquinone and the double bond of maleic anhydride. Norton quotes as authority a paper by Diels and Alder (1929) to which is attributed also an unlikely proof of the structure of the adduct. Perusal of this paper, however, fails to reveal any mention of adduct formation with anthraquinone, and as far as we can discover the subject is not mentioned in any of the works of Diels and Alder. Norton refers also to an observation by Morrell and Samuels (1932), who, in an account of an unrelated investigation, briefly mention that no reaction takes place between maleic anhydride and anthraquinone. These authors make no reference to any previous work on the subject.

In view of the theoretical interest of such a reaction, the following experiments were undertaken in an attempt to isolate an adduct. A range of temperatures was employed since equilibria in adduct formation are considerably affected by temperature. (Bachmann and Kloetzel, 1938.)

(1) A solution of anthraquinone (2 g.) and maleic anhydride (10 g., molar ratio 10 : 1) in benzene was refluxed for eight hours.

(2) A solution of anthraquinone (2 g.) and maleic anhydride (10 g.) in nitrobenzene was refluxed for two hours.

(3) A melt of anthraquinone (2 g.) and maleic anhydride (10 g.) was held at 200 for two hours.

In all cases both the anthraquinone and the maleic anhydride (as maleic acid) were recovered almost quantitatively and no indications of adduct formation could be found. It is concluded, therefore, that anthraquinone does not react with maleic anhydride in the Diels-Alder reaction.

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CONTRIBUTIONS TO THE STUDY OF THE MARULAN BATHOLITH.*

PART I. THE CONTAMINATED GRANODIORITES OF SOUTH MARULAN AND MARULAN CREEK.

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With Plates VIII, IX.

Manuscript received, May 12, 1948. Read, July 7, 1948.

CONTENTS.

INTRODUCTION.

The Marulan batholith is a composite intrusion outcropping over a large area which trends more or less northward from the Bungonia-Marulan district towards Wombeyan Caves. It has been the subject of considerable attention at intervals throughout more than forty years (see Woolnough, 1909; Osborne, 1931; Naylor, 1939), but detailed studies upon it are still in progress. Naylor was of the opinion that the intrusion was probably to be assigned to the Late Middle Devonian diastrophism, and when one considers the question of age comparatively in the light of our knowledge of the major Palæozoic tectonic episodes in eastern Australia, there seems little doubt that Naylor's view is correct.

It is clear to the writer that the only satisfactory way to elucidate the geological history and petrological evolution of this batholith is by carrying out detailed petrological investigations upon the relations of the various components, including studies in hybridism and in the contamination by country-rock, which is so widely present throughout the mass.

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* The author gratefully acknowledges financial help from the Commonwealth Research Grant in connection with this work.

Various members of the Marulan batholith have been contaminated by the sedimentary rocks through which it has broken. Due to the varied *terrain* invaded by the complex, there is a considerable range of assimilation-effects. The Silurian limestones of South Marulan provide a striking endogenic reaction, and the Ordovician slates and phyllites of the eastern part of Glenrock Estate have also played an interesting part in a series of reactions with the granodiorite. We shall examine these two cases in this paper.

GRANODIORITE CONTAMINATED BY LIMESTONE AT SOUTH MARULAN.

The general relations of these rocks to the associated exogenic zone has been figured and described by the writer in another paper (1931). A brief description of the contaminated granodiorite was given, but more chemical work has now been done on the problem and the present communication supersedes the earlier statement.

Skarns are intimately associated with the altered granodiorite and it is really difficult sometimes to separate the two groups. This is due to the following sequence of processes having operated:

(*a*) Crystallization of contaminated magma.
(*b*) Limited pneumatolytic activity.
(*c*) Hydrothermal action contemporaneous with skarn development.

The last-named processes, while responsible for the metasomatism of calcite, also altered the contaminated rocks, strongly.

These rocks, as a whole, have an igneous aspect, being dark in colour and showing abrupt textural variations. They are cut by aplitic and quartzose strings and veins, and also with prehnite. The last-named occurs as a constituent of some of the rocks, but its presence in veins is due to epigene action.

Unfortunately a complete gradation between granodiorite and modified rock is not traceable, but after the intervention of some soil the contaminated rocks are found about 35 feet from the pure granodiorite. There is no doubt whatever that the latter is the parent or unaltered type. For so large an intrusion as the Marulan batholith the endogenic zone at South Marulan is quite narrow.

Towards the junction of exogenic and endogenic zones the contaminated types become coarser than elsewhere and the dark constituents show idiomorphic character making them conspicuous against the lighter ground of felspar or prehnite. Erratic variations in the proportions make for inhomogeneity, and altogether the lithology is distinctive. The rocks can best be dealt with as follows:

(*a*) Contaminated granodiorite, generally hydrothermally altered.
(*b*) Pyroxenites.
(*c*) Diopside-prehnite rocks.

PETROGRAPHY.

(*a*) *Normal Granodiorite* (*Basic Variety*).

This rock is fairly even and medium grained, and presents little of special interest except that it is more basic than the bulk of the Glenrock mass. Nevertheless, it represents the uncontaminated magma of this district. The minerals present are plagioclase, orthoclase, hornblende, biotite, quartz, sphene, apatite, magnetite, zircon and pyrites. The plagioclase is zoned, An_{40} to An_{25}, the central zones being altered to sericite, calcite, kaolin and zoisite. Poorly cleaved and cloudy potash felspar and interstitial quartz are present. The biotite has weathered to chlorite, and notable amounts of secondary sphene, and occasionally sericite, form inter-cleavage masses. Hornblende is weakly pleochroic with X=pale straw-coloured, Y=brownish green and Z=light brown, $Y \gg Z > X$.

The extinction is $\widehat{Zc}=14^\circ$. Decomposition to chlorite is fairly prevalent. The fabric is monzonitic, the orthoclase and quartz being completely xenomorphic. There is no pyroxene in the normal rock from this locality. An analysis of the granodiorite is given below.

SiO_2	57·66
Al_2O_3	17·36
Fe_2O_3	6·54
FeO	0·94
MgO	4·07
CaO	7·28
Na_2O	1·56
K_2O	1·38
H_2O	2·24
H_2O	0·20
CO_2	abs.
TiO_2	0·55
P_2O_5	0·14
MnO	0·04
	99·96

Norm.	
Quartz	17·28
Orthoclase ..	8·34
Albite	13·10
Anorthite	35·31
Corundum ..	0·41
Hypersthene ..	20·36
Magnetite ..	1·39
Apatite	0·40

Sp. Gr. = 2·82 Normative plagioclase, $Ab_{27}An_{73}$

Granodiorite, South Marulan. Anal. W. H. Herdsman.

(*b*) *Contaminated Granodiorite.*

The outstanding feature in these rocks is the abundance of well-developed diopside-hedenbergite crystals which are prismatic up to a maximum length of 5 mm. Grey in thin section they show good cleavage and much twinning. The general properties are very close to those of the pyroxene in the rocks of group (*c*), the chief difference being in a higher diopsidic content, the extinction being $\widehat{Zc}=39^\circ$. The other minerals are plagioclase (now much altered), microcline-microperthite, idiomorphic sphene with occasional ilmenitic nuclei, prehnite, clinozoisite and apatite. Frequently the only indication of plagioclase are the outlines of pseudomorphs, but in a few places its composition is determinable at approximately an average of An_{50}. The decomposition of plagioclase has yielded scapolite, calcite, zoisite, sericite and kaolin, some of these being due to pneumatolytic and hydrothermal action. Potash felspar locally increases in some rocks where quartz is also developed, and these are clearly due to infiltration and related to the pegmatitic material veining the contact. Clinozoisite has characteristic interference colours and strong cleavage. The sphene is noticeably pleochroic with the following scheme: X = pale yellow, Y = pale greenish yellow, Z = reddish brown, $Z \gg Y > X$. Interference figures bespeak a small optic axial angle. The prehnite in these rocks is deuteric in origin; it shows general turbidity and the typical features of aggregate extinction, etc., so common in this mineral.

(*c*) *Pyroxenite.*

Some parts of the contaminated mass are composed almost entirely of diopside-hedenbergite so that the rock may be termed pyroxenite. The specimens pass eventually without sharp junctions into the other types. Although not abundant, these rocks may be obtained in specimens up to one foot in diameter. The pyroxene is a little more ferriferous than that in the previous groups of rocks, and its optical properties and composition are shown hereunder.

	(3)	(1)	(2)	Metal Atoms on Basis of 6 (O).	
SiO_2 ..	50·91	49·48	50·28	1·962	1·99
Al_2O_3 ..	0·17	1·17	1·19	·028	
Fe_2O_3 ..	·76	·14	·15	·002	1·019
FeO ..	17·34	16·52	16·80	·545	
MgO ..	7·21	7·13	7·25	·423	
MnO ..	·21	·60	·60	·018	
TiO_2 ..	—	·40	·41	·011	
CaO ..	22·93	23·59	23·32	·973	·973
P_2O_5 ..	—	·64	—		
H_2O ..	—	·10	—		
	99·53	99·77	100·00		

$(Ca, Mg, Fe'', Fe''', Mn, Ti)_2(Si, Al)_2O_6$

2V (+) Medium
$\widehat{Z c}$ =47°
α =1·698
β =1·705
γ =1·720
γ-α =0·022
Fe/Mg=3·02

1. Diopside-hedenbergite from pyroxenite, Sth. Marulan. Anal. Naima Sahlbom.
2. The same, after deducting apatite and water.
3. Pyroxene, Nordmark, Sweden. (Iddings Rock Minerals, p. 300.)

The analysis shows the mineral to be a normal member of the diopside-hedenbergite series with molecular constitution such that He/Di=58·39. The mineral has little titanium which belongs to the Y group entirely.

The similarity of the Marulan and the Swedish minerals is very noticeable, and it is to be remarked that they occur with somewhat similar parageneses.

On the other hand the pyroxene from pyroxenite in the endogenous contact at Scawt Hill (Tilley, 1929) is more diopsidic, the ratio Fe/Mg being 0·71.

The Marulan pyroxene is low in alumina and thus is in contrast with the type of aluminous pyroxene which Tilley (1938) has shown to be characteristic of some limestone contacts. In some of these cases at least the associations are different from that of Marulan in that the pyroxenes come from exogenic contacts and have not been precipitated from magma.

The accessories in the pyroxenic rocks which rarely aggregate more than 3% are sphene, apatite and a little turbid felspar.

(*d*) *Diopside-prehnite Rocks.*

These occur with either of the foregoing in the most irregular fashion. They consist of diopside-hedenbergite and prehnite with a few accessories comprising apatite, sphene, a little potash felspar and some introduced quartz.

The prehnite, which is primary, occurs in well cleaved plates and sheaf-like masses, these being for the most part quite clear. Contiguous with such material there is a good deal of very turbid prehnite, and the two varieties grade into one another. The mineral shows shadowy extinction, good cleavage, and has a noticeably small (+) 2V, while the sign of the elongation varies.

The diopside, which is identical with that in rocks of group (*b*), may be so well developed as to cause the prehnite to be relegated to an intergranular position, or alternatively the small idiomorphs of pyroxene may lie embedded, poikolitically, in large masses of prehnite. A certain amount of excess calcite is often seen.

Chemical Discussion.

The contaminated rocks are the result of precipitation from a modified magma ; they are not related to the pure granodiorite in the sense that reaction made over such a rock into a contaminated product. There is no sign, for example, of " regenerative crystallization " in the sense put forward by Kennedy and Read (1936). Lime-enriched liquid, which was being depleted in other constituents, began to crystallize as pyroxenite, and later continued on with the formation of the other types already described.

The study of the pyroxenes indicates that the variety in the pyroxenites is more ferriferous than any in the surrounding rocks. Although no analysis of the contaminated rock is available, the knowledge of the general modal percentages (by volume) allows us to conclude that in a contaminated type with 45–50% of diopside the proportion of FeO in the rock would be approximately equal to the percentage in the pure granodiorite (see above).

The composition of the pyroxenite must be almost the same as that of the pyroxene. As stated, the Fe/Mg ratio in the latter is 3·02, while in the pure granodiorite it is 2·17. Thus the pyroxenite is partly due to a local concentration of iron at the expense of MgO. This has led to an enrichment of the neighbouring magma in MgO at least, and possibly in other oxides. Some of the magnesia freed by the increase of the hedenbergite molecule in the pyroxene has been fixed in diopside in the lime-silicate rocks, and the rest has helped to build the slightly more diopsidic pyroxene of the contaminated granodiorite. While the crystallization of the pyroxenite and granodiorite was in progress some constituents were migrating to the exogenic zone. Earlier study of that zone has shown that considerable amounts of silica and alumina, some magnesia and small quantities of iron and potash left the magma for the limestone. Nothing but lime was received in return, which was instrumental in effecting a conversion of the hypersthene molecules of the granodiorite (see norm) into diopside-hedenbergite molecules.

Now if we eliminate the infiltrated quartz and orthoclase from these rocks and ignore the pneumatolytic and deuteric action, we see that the granodiorite magma with the abovementioned oxides removed, would approximate to a liquid which would produce by crystallization a monzonite or diorite-gabbro. The addition of lime has been to modify such a magma to a composition which would determine the separation of abundant diopside-hedenbergite, as the first of a new reaction series. The continual supply of lime led to the combination of the whole of the (Mg, Fe)O available, and further promoted the growth of idiomorphic sphene, the TiO_2 of the magma being shared between this mineral and the diopside. After most of these minerals had developed the alumino-silicates separated, the plagioclase preceding the microperthite. The lime-soda felspar was not labradorite and the slightly perthitic potash-felspar received its soda according to one of two sets of conditions ; either (*a*) the basification and diminution in volume of the plagioclase led to a little surplus Na_2O, or (*b*) in the gradual depletion of the magma in alumina (due to its migration to the limestone) that which was left united with potash because of strong affinity with this alkali, and thus labradorite could not continue to form, and any soda left was taken up in perthite. A corollary, under normal conditions, of this would be zoning of the plagioclase to give a more acid periphery, but this was prevented by the onset of pneumatolytic and deuteric activities which allowed the water of the magma to become effective, and prehnite and other hydrous alumino-silicates were formed. Scapolite and sericite were also produced in some quantity and a good deal of kaolin developed. Some structural changes, chiefly in the nature of shrinkage-effects, made possible the invasion of salic liquid, and this is expressed in the acid veins and strings to be seen through all rocks.

Such is the probable evolution of the contaminated rocks of groups (*b*) and (*c*). It only remains to explain that the primary prehnite of the diopside-prehnite rocks took the place of labradorite when circumstances were such that insufficient alumina was available for practically any felspar to form, and (OH) was active.

We see, then, that a profound change in the molecular constitution took place in the altered granodiorite magma and the trend of crystallization was radically altered from the normal granodiorite sequence, chiefly due to the following factors:

(*a*) Subtraction of SiO_2, Al_2O_3, MgO and K_2O.
(*b*) Addition of lime.
(*c*) Concentration of iron in a lime-enriched magma resulting in pyroxenite crystallizing.
(*d*) Onset of pneumatolysis and later hydrothermal activity in which water played a leading part.

The relations of the combinations of the oxides in the unaltered and contaminated rocks is shown in a summarized form on page 122.

GRANODIORITE CONTAMINATED WITH SHALE-CALCIC HORNFELS, ETC.

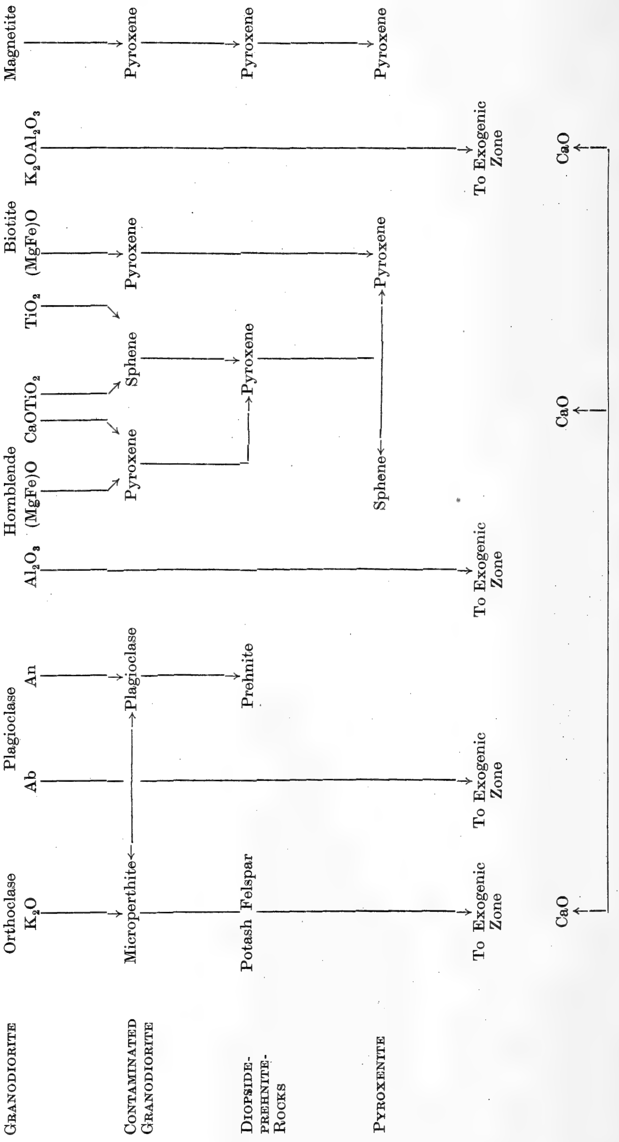
Field Occurrence.

The greater part of Glenrock Estate, south-east of Marulan, is given over to granodiorite now exposed on the plateau surface and in the gorge of Barber's Creek and the tributary stream beds, which are mostly on the tableland. An examination of the granodiorite throughout the Glenrock area leads one to conclude that a considerable portion of the rock is contaminated by sedimentary material and also that the last episode in the crystallization history of the mass has been a fairly strong deuteric activity. The presence of rhombic and monoclinic pyroxenes in the granodiorite was recorded by Woolnough. It is significant that in the areas where the granodiorite is pyroxene-free there is an absence of evidence of contamination, such as inhomogeneity, " strew " from digested xenoliths, and in general a minimum of hydrothermal products. In particular the mineral epidote, which is abundant in the deuterically altered phases and in the aplites and pegmatites, is rarely seen. Again, any xenoliths present show very little reaction. All these features suggest that more advanced contamination was made possible because of conditions of relatively low temperature and abundance of volatiles just at the close of the pneumatolytic stage. These conditions obtained at least on the eastern margin of the complex.

The prevalence of contamination effects in the rocks of Glenrock Paddock and the great abundance of inclusions with reaction rings along the eastern side of the complex confirms the suggestion of Woolnough (1909, p. 786) that the present ground-surface is not greatly removed from the former rather flat upper surface of the batholith.

It is not within the province of this paper to deal with the petrogenetic problems of the granodiorite, but to consider the reaction between it and several types of hornfelses which occur as xenoliths.

In Marulan Creek near where it begins to descend through a tributary gorge to Barber's Creek there are excellent exposures of the contaminated and xenolithic mass. Here one is near the margin of the batholith where the fragments of country rocks are very abundant. The granodiorite forming the host to these is variable in texture, and is seamed with streaky as well as sharply bounded veins of aplitic and pegmatitic material. In these orthoclase reaches a large pro-



N.B.—Quartz is omitted from the scheme.

portion of the whole, and epidote is common. The latter has been the last mineral to crystallize, filling druses in the central parts of the veins. Beautiful dark green crystals are frequently to be seen.

The inclusions are of all sizes up to about one foot in diameter, and show more or less rounded outlines in the majority of cases. Sometimes where injection of magma has taken place along bedding planes there has been early disintegration before reaction and angular fragments often persist. At other times perfectly rounded contours give rise to spheroids.

In almost every case the xenoliths are surrounded by well-defined reaction rings which vary greatly in thickness. This variation appears to be related to the size of the fragment and the availability of volatiles for the reaction process. The appearance of the inclusions with their coronæ of more salic minerals is very characteristic. The rings have a predominantly pink colour due to the abundance of felspar which has weathered more readily than that in the parent rock.

Examining the reaction rings more closely one sees that almost invariably there are three zones between the main portion of the inclusion and the relatively unaltered granodiorite. Succeeding the main mass of the inclusion, near its margin there is the following sequence:

(*a*) A narrow zone of greenish-grey material of very fine grainsize.
(*b*) A still more restricted zone of speckled material in which hornblende is discernible.
(*c*) A medium-grained igneous zone consisting of abundant felspar and quartz with some hornblende or chlorite.

In some inclusions the zone (*b*) is not easily distinguished, but it is generally apparent under the microscope. A photograph (see Plate VII, fig. 4) shows a typical inclusion with reaction ring. A certain amount of injection of the marginal zone of the inclusion is also shown.

The width of the reaction areas may be as much as three inches in xenoliths of about eight inches diameter.

The weathering of the xenolithic granodiorite varies for some reason not yet apparent. Generally the surface of parent rock and xenolith is uniformly eroded, but in places (e.g. in Marulan Creek near Portion No. 19) the xenoliths have been responsible for a nodular structure which gives the rock the appearance, in the distance, of a differentially weathered conglomerate. In this type it is necessary to break open the resistant reaction material of the spheroids before the nature of the xenolithic nucleus can be examined.

PETROGRAPHY.

(1) *The Least Modified Granodiorite.*

In view of the uncertainty as to whether any of the granodiorite in the neighbourhood of the inclusion zone is uncontaminated, we shall employ the adjective "least-modified" here for the material definitely distinct from the endogenic reaction rings.

W. G. Woolnough gave a good account of the granodiorite from Glenrock Falls (which are near the area of contamination), and recorded the presence of both diopside and hypersthene. The analysis from Woolnough's paper shows distinct differences from the analysis (given above) of a somewhat basic phase of the granodiorite. This basic phase is regarded here as the equivalent of the unaltered rock of the Glenrock Estate. The former analysis appears to bear a similar relation to the latter as does an analysis (given below) of the modified granodiorite of Marulan Creek.

Almost all the slices of granodiorite examined show much evidence of hydrothermal alteration. This, it is believed, followed the reaction which took place between magma and hornfels.

The minerals seen under the microscope are *plagioclase*, *potash felspar*, *amphibole*, *biotite*, *quartz*, *magnetite*, *apatite*, *zircon*, and a good deal of *chlorite* of varying colour, and significant *epidote*.

The *plagioclase*, which is strongly zoned, is difficult to determine, but the average composition is from An_{50} to An_{25} for the main part of the crystal, while the outermost zones are of clear andesine-oligoclase. The alteration products are kaolin, epidote, scapolite and calcite.

The *potash felspar* is slightly perthitic at times, but otherwise appears to be orthoclase, and is always heavily kaolinized. The *amphiboles* are in confused groups of subidiomorphs showing remnants of twinning. There are at least two varieties. One is pale green to grey and has $Z\hat{}c=14°$, while the other is finely fibrous and of darker green colour, and shows the properties of uralite. The whole of the aggregates show patchy coloration and extinction, and there are evidences of volume changes consequent upon hydrothermal action. The pale variety is sometimes close to tremolite in composition. Its R.I. is $\beta=1\cdot661$.

Biotite is reddish-brown with epidote, sericite and sphene as alteration products along the cleavage, while extensive change to chlorite is seen throughout most of the flakes. In fact chlorite is one of the most characteristic constituents of all the rocks in the eastern side of the Marulan complex. The deposition of epidote and sericite in the cleavages with bending of the cleavage planes due to volume changes is distinctive, and forms a useful feature when comparison of modified hornfels and granodiorite is investigated. The biotite has $\beta=1\cdot643$.

Quartz is interstitial and shows fluid inclusions. The fabric of the rock is subidiomorphic granular to sub-monzonitic.

(2) *The Xenoliths.*

There is not a great variety amongst the inclusions. They are clearly the thermally metamorphosed equivalents of Ordovician slate and quartzite, and occasionally of calcareous shaly material.

Some interesting study is to be had from the standpoint of the thermal metamorphism of these types, but that will not be dealt with here. It is sufficient to point out that under the conditions of sudden elevation of temperature and relatively quick cooling, the small fragments immersed in a magmatic medium have recrystallized, sometimes giving unstable assemblages in which extra phases are present above the number expected under equilibrium conditions. The types examined in order of abundance are:

(*a*) Andalusite-cordierite-spinel-plagioclase hornfelses.
(*b*) Sandstone hornfelses.
(*c*) Cordierite-hypersthene-plagioclase-spinel hornfelses.
(*d*) Hypersthene-diopside-plagioclase hornfelses.

(*a*) *Andalusite-cordierite-spinel-plagioclase Hornfelses.* In these rocks sillimanite may occur in fair abundance along with the other minerals. In all rocks orthoclase is an important consitutent. Biotite is absent from the central parts of xenoliths and develops near to the reaction border. Until further work is done upon the group of hornfelses as a whole it is not possible to decide whether some of the biotite-bearing rocks owe their mica purely to thermal change or to the effects of magmatic reaction. In this section the rocks which clearly show biotite as a product of reaction are considered.

The rocks are very fine grained and have a resinous lustre. The minerals present are cordierite, orthoclase, plagioclase, andalusite, pleonaste, magnetite, zircon and perovskite. *Cordierite* is abundant in twinned and ragged units, which are strongly sericitized or pinitized. Haloes around zircon are very well developed. *Andalusite* is xenoblastic, and has many inclusions. The *spinel* is very subordinate and is associated with magnetite. The *plagioclase* is andesine, and is never abundant. *Orthoclase*, on the other hand, is prolifically developed.

As the magmatic contact is approached the cordierite shows more alteration, sometimes to a yellow isotropic mass, and eventually fails, and biotite begins to make its appearance. It is generally found intimately connected with iron ore and spinel. It has the same general colour and refraction of the biotite of the granodiorite, and also shows in places the peculiar intercleavage masses of epidote or sericite which are found in the igneous rock.

In the greyish-green zone the potash felspar is now strongly kaolinized and plagioclase has become acidified so as to be almost pure albite, although it is also decomposed. The iron ore decreases and andalusite disappears. A considerable amount of granular epidote is found through the turbid zone.

The stages of development of biotite from cordierite and iron ore, involving also probably the using up of the small amount of spinel present, can be seen in the inner border of the turbid zone. Partly chloritized cordierite merges into olive-green biotite which, with incorporation of more iron, becomes brownish and eventually is similar to the mica in the granodiorite. In some of the modified hornfelses the plagioclase is a little more basic than in the unaltered rock. Whether this is due to an original higher calcic character or not is difficult to determine.

At this stage the reciprocal changes were " arrested " by congealing of the magma and further development was in the nature of a deuteric hydration.

In the granodiorite the change in the neighbourhood of the inclusions is easily perceived and needs little description. A slight concentration of quartz and felspar and a decrease of femic material are the chief features. The felspar is partly plagioclase, but mostly orthoclase. The magma therefore is definitely depleted in ferromagnesian content and receives additional potash. Some analyses dealing with this reaction are given in Table 1.

(*b*) *Sandstone Hornfelses.* The prevalence of quartzites in the Ordovician rocks of the district leads to the relative abundance of gritty and quartzitic hornfelses in the xenoliths. The central parts of such inclusions show grains of *quartz* and a little *alkali-felspar* cemented by chloritic material which, under high magnification, appears to have been partly recrystallized into *biotite* and *cordierite* which has iron ore inclusions. The quartz and felspar may have recrystallized, but this is not absolutely clear. The effect of the immersion in magma has been to increase the biotite content due partly to addition of potash and partly to crystallization of detrital material. The change in the magma appears to be practically nil.

(*c*) *Cordierite-spinel-hypersthene-plagioclase Hornfelses.* These have fairly coarse grainsize, the *cordierite* and *plagioclase* reaching a maximum of 3 mm. diameter. The former is not altered greatly and shows strong chequer-twinning. The plagioclase is labradorite (about An_{52}) with finely drawn albite twinning. *Hypersthene* is rather striking with pleochroism, X=wine coloured, Y=greyish yellow, and Z=greyish green, and is in extremely irregular grains suggesting low crystalloblastic position.

These hornfelses are only slightly deficient in silica for the *spinel* is very subordinate, occurring as dark blebs and strings through plagioclase. There is no orthoclase in the typical rock, and no thermal biotite.

The changes in this type of xenolith as the granodiorite is approached are very interesting. Hypersthene, with its iron-ore clots, begins to change to a pale pyroxene, then to green hornblende and eventually to olive green biotite. The last-named sometimes develops directly at the expense of the iron ore and pyroxene. In this case potash must come from the magma, as it is not available in the hornfelses. The cordierite, unlike that in rocks of group (*a*), does not go over to biotite so readily, due perhaps to the role being played by hypersthene and to the dearth of potash. It appears to change to sericite and then to disappear when green hornblende develops along the periphery of the inclusions. This hornblende is idiomorphic, shows a greenish blue colour, and has the extinction angle of an actinolitic variety, $Z \hat{} c=18^{\circ}$. Spinel disappears on the addition of quartz or at the growth of biotite, and the plagioclase is acidified in this case—a feature somewhat contrasting with the plagioclase in rocks of group (*a*). There is less orthoclase in this turbid zone and the rather abrupt succession of

(i) Cordierite-spinel-hypersthene-plagioclase,
(ii) Plagioclase-cordierite-biotite
(iii) Plagioclase-quartz-orthoclase-hornblende

shows clearly the state of inequilibrium when the reactive processes were arrested.

In the magma, as a result of a concentration of hornblende at the margin of the inclusion, there is a general increase in salic constituents. Deuteric activity has caused the change from hypersthene to bastite. No analysis for these reactions is available.

(*d*) *Hypersthene-plagioclase-diopside Hornfelses.* These belong to a more calcic type, of which a few representatives are seen. They have a little orthoclase but no original biotite. As indicated below, all the biotite is due to reaction. *Diopside* is almost colourless, occurring in stout prisms set in *plagioclase* which is poorly twinned and slightly zoned and has a composition of basic andesine to acid labradorite. The *hypersthene* is present in rounded grains arranged in groups and strings. It is dark brown and shows fairly strong pleochroism, and is associated with iron ore.

The effect of the magmatic environment has caused a very decided change in the rhombic pyroxene, but not in the diopside. The former passes to a pale diopsidic type and then to leek-green hornblende and finally to olive-green biotite. The diopside remains right up to the border zone and then only sluggishly reacts to give some biotite if iron ore is available. Orthoclase is now wanting and there is a good deal of more acid plagioclase. The effect of the later deuteric solutions has been to give much epidote and some kaolin in the peripheral zone of the xenoliths.

The magma has experienced much the same modification as detailed in the last subsection. A migration of potash and quartz has led to enrichment in quartzo-felspathic constituents at the junction.

Chemical Discussion.

In Table 1 are given analyses of (1) a cordierite-andalusite-spinel-plagioclase xenolith, (2) an altered xenolith which had developed a certain amount of biotite and hornblende, (4) modified granodiorite from the neighbourhood of the inclusions, and (5) a basic phase of the granodiorite (already discussed in last section).

In regard to the comparison of (1) and (2), it is to be remarked that on account of the uniformity of texture and general constitution of the hornfelses of type No. (1) the selection of a rock which has been in the general condition of (2) is justified. Each rock having been solid at the time of immersion in magma, it is possible to compare volumes, based on densities. This has been done (see Table 1).

It will be seen that the most important changes are as follows :

The xenolith has given alumina, titanium and potash to the magma, and has gained significant CaO, MgO, iron and Na_2O.

The actual amounts shown in Table 1 must not be taken into account so much as the qualitative effect of the changes, as indicated by the chemistry and petrography of the study. Thus when viewing the changes in the magma by inspection of (4) and (5) we note that the concentration of alkali felspar around the inclusion is indicated in the higher values, in (4), for silica and alkalis, the alumina having been more than sufficient to satisfy the increases of Na_2O and K_2O. On the other hand there is a distinct decrease in MgO, FeO and CaO, and this is correlated with the changes in the xenolith.

TABLE 1.

	(1)	(2)	(3)	(4)	(5)
SiO_2 ..	51·68	51·37	51·92	61·96	57·66
Al_2O_3 ..	25·86	22·96	23·21	15·82	17·36
Fe_2O_3 ..	0·48	1·70	1·72	1·56	0·94
FeO	6·63	5·92	6·01	4·60	6·54
MgO ..	3·29	4·31	4·36	3·26	4·07
CaO	0·61	2·02	2·04	4·84	7·28
Na_2O ..	2·82	3·38	3·41	2·17	1·56
K_2O ..	5·18	4·77	4·82	2·48	1·38
H_2O ..	2·28	2·65	2·68	2·25	2·24
H_2O- ..	0·10	0·10	0·10	0·16	0·20
TiO_2 ..	0·72	0·59	0·60	0·52	0·55
MnO.. ..	tr.	tr.	tr.	0·05	0·04
P_2O_5.. ..	0·06	0·12	0·12	0·15	0·14
CO_2 ..	0·12	abs.	—	abs.	abs.
	99·83	99·89	100·99	99·82	99·96
Sp. Gr. ..	2·72	2·75	2·75	2·76	2·82

Normative plagioclase, $Ab_{43}An_{57}$ $Ab_{27}An_{73}$.

1. Andalusite-cordierite-spinel plagioclase xenolith. Marulan Creek.
2. Modified inclusion, Marulan Creek.
3. No. 2 recalculated for comparison with No. 1.
4. Modified granodiorite near hornfels xenoliths. Marulan Creek.
5. Granodiorite (basic phase). Sth. Marulan.
Anal. for all rocks, W. H. Herdsman.

Norms.

	(4)	(5)
Quartz	21·12	17·28
Orthoclase ..	15·01	8·34
Albite	18·34	13·10
Anorthite	23·35	35·31
Corundum ..	0·92	0·41
Hypersthene ..	14·44	20·36
Magnetite ..	2·32	1·39
Ilmenite	0·34	1·06
Apatite	0·91	0·40

Here we must be careful to allow for deuteric phenomena in so far as we can determine its mineralogical effects. It appears from microscopic study that the hydrothermal alteration was essentially a hydration, plus a certain amount of albitization, and thus we cannot be sure how much of the excess soda (if any at all) is due to reciprocal reaction before deuteric change. In view of the general principles of contamination it appears likely that the increase of soda, in the xenolith, is apparent and not real. The problem of the interrelation of the deuteric and reactive modifications in magma and inclusion enhances the interest of the present study.

Mineralogical Changes.

Mineralogically we see that the chief rearrangements have been as follows :

(*a*) Cordierite, spinel, iron ore and orthoclase have reacted with water and possibly MgO from the magma to give biotite. Sufficient potash in the inclusion (originally 5·18%) allowed enrichment of magma in orthoclase.

(*b*) Hypersthene and diopside have given rise to biotite either direct, or through hornblende, the other reacting components coming from the magma, particularly lime and water.

(*c*) The part played by the plagioclases is not clear. The acidification which went on in the turbid zone and the concentration of alkali-felspar in marginal magma-zone are partly due to deuteric solutions. It is probable that if the plagioclase of the inclusion were about the same composition as that of the granodiorite, any activity by CaO would be directed to building hornblende.

(*d*) The hornblende in the outermost zone of the inclusions indicates the "convergence" which has marked the processes. The goal for the inclusions is determined by the constituents of the granodiorite. It is significant that only one portion of the "convergence field" was reached by the components of the inclusions, that is the range of the ferromagnesian constituents. Later action would have been in the direction of producing convergence in the matter of the felspar series.

It is seen, therefore, that a rather unbalanced set of transfers operated, but this really emphasizes one of the main advantages of the present occurrence, viz. that the conditions indicated by the assemblages were of a preliminary character when equilibrium had not been established. Thus these rocks give us information about some of the intermediate steps leading to the establishment of reciprocal changes in which definite associations of components are wrought.

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EXPLANATION OF PLATES.

PLATE VIII.

Fig. 1.—Granodiorite (somewhat basic phase) from South Marulan near contaminated zone. Altered plagioclase crystals, subordinate orthoclase, quartz and considerable ferro-magnesian content. Hornblende is subidiomorphic, and biotite shows inter-cleavage mass of epidote. Ordinary light × 18.

Fig. 2.—Diopside-prehnite-orthoclase rock, due to contamination of granodiorite, South Marulan. Crystals of pyroxene associated with intensely kaolinized orthoclase and shapeless masses of prehnite which is deuteric in origin. Ordinary light × 18.

Fig. 3.—Diopside-prehnite rock, South Marulan. Crystals of diopside-hedenbergite are set within masses of prehnite. Note characteristic variable turbidity of the latter mineral. Ordinary light × 18.

Fig. 4.—Pyroxenite from South Marulan. The rock is composed almost entirely of diopside-hedenbergite in well-formed crystals, the accessories being sphene, ilmenite and prehnite. (Rock due to contamination.) Ordinary light × 18.

PLATE IX.

Fig. 1.—Modified granodiorite from Marulan Creek. Concentration of Q, Hb and Or near reaction zone is indicated. Ordinary light × 18.

Fig. 2.—Diopside-hypersthene-plagioclase. Abundant dark Hy, paler Di and larger P. Loc., Marulan Creek. Ordinary light × 18.

Fig. 3.—Modified cordierite-hypersthene-plagioclase-spinel rock. Pronounced development of biotite. Xenolith at Marulan Creek. Ordinary light × 18.

Fig. 4.—Hornfels xenolith in granodiorite. Reaction is well shown, also initial marginal disintegration. Three-quarters natural size.

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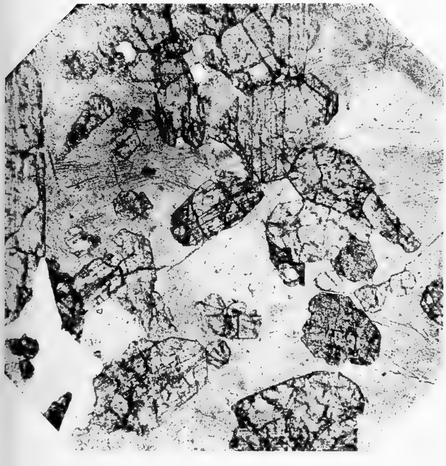

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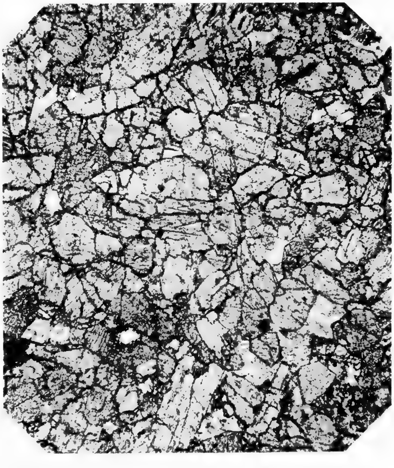

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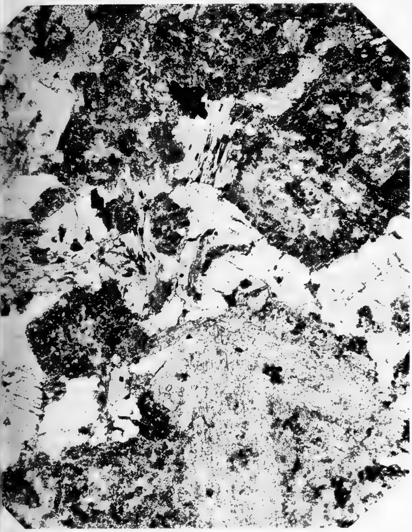

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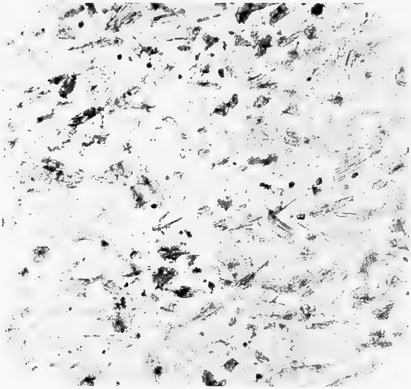

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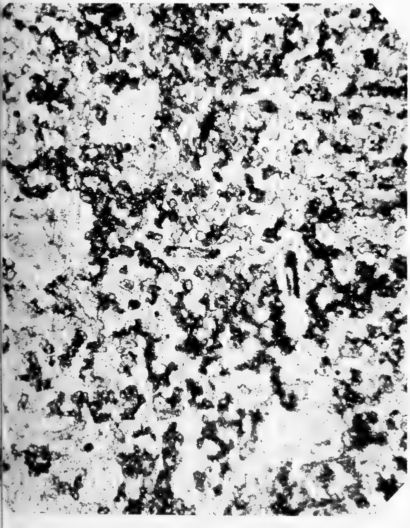

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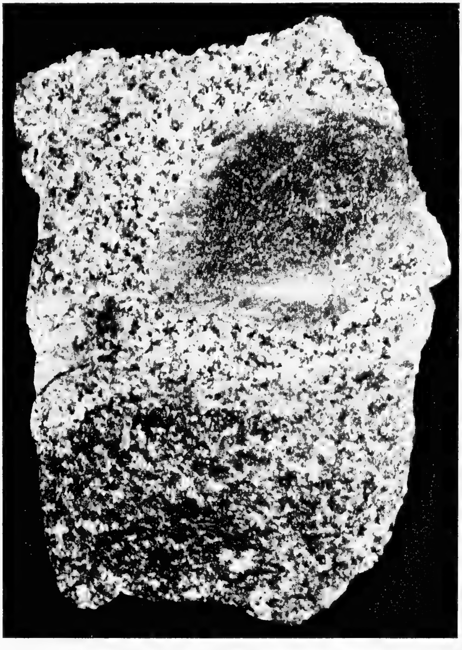

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NITROGEN IN OIL SHALE AND SHALE OIL.

V. The Determination of Nitrogen in Shale Oil and Oil Shale.

By Geo. E. Mapstone, M.Sc., A.A.C.I., M.Inst.Pet.

Manuscript received, June 2, 1948. Read, July 7, 1948.

Introduction.

The application of the Kjeldahl method for the determination of the nitrogen content of crude petroleum and crude shale oil has been attended by difficulties which appear to have been due mainly to the failure to appreciate fully the various factors involved. For example, when determining the nitrogen content of crude shale oil, Petrie (1) found that twenty days' digestion with sulphuric acid were necessary before the mixture cleared. Since that time, however, catalysts have been used together with added sodium or potassium sulphate in order to speed up the digestion.

The U.O.P. method for the determination of nitrogen in petroleum (2) recommends the continuation of the digestion for from one-half to five hours after the acid clears, but gives neither a reason of the extended time nor any indication of its importance. This method is a simple adaptation of the first successful application of the Kjeldahl method for the determination of nitrogen in petroleum by Poth *et al.* (3). These workers used a mercuric oxide-copper sulphate catalyst with potassium sulphate to raise the temperature of the digestion mixture, and they found that, in order to recover all the nitrogen present, it was necessary to continue the digestion for five hours after the acid had cleared.

Shale Oil.

This method was modified slightly by reducing the scale of the analysis, and then used as a basis for the determination of the optimum conditions. All aspects of the method were checked in order to render its application as accurate and as simple as possible.

Digestion.

With the shale oil it was found most convenient to use approximately two grammes of the sample, as the use of a larger sample gave difficulty with foaming during the digestion, while a smaller sample gave insufficient ammonia on the final distillation. The addition of some paraffin to the digestion mixture, as recommended by U.O.P. to reduce foaming, was found to be quite ineffective.

Samples of crude shale oil were digested for varying times in order to determine the optimum digestion time. It was observed that the time required for the digestion mixture to clarify was not significant, the significant time being that for the subsequent digestion. This result is at variance with Crossley's observation (4) that maximum nitrogen figures were obtained with the minimum heating rate to give the minimum " clearing " time. Subsequent work has, however, indicated that excessive " clearing " times can give low results, but not if the heating is carried out as described in the final method. The results of these tests (Table 1) show that a minimum digestion time of 1½ hours after clarification is necessary. A digestion time of two hours after clarification of the acid was therefore taken as standard.

It is possible that the very slightly lower value obtained after three hours' digestion was due to the volatilization of part of the ammonium sulphate. This explanation was suggested by the observation that if much sulphuric acid was allowed to distill from a sample during the digestion a low, and sometimes negligible, result was obtained. Beet and Furzey (5) also observed that prolonging the digestion much beyond the minimum time required for complete conversion of the nitrogenous material to ammonia was liable to give slightly low results.

TABLE 1.

Effect of Digestion Time on Result.

Digestion Time After Clearing.	Observed Nitrogen Content Percentage.
0 hour	0·393
½ hour	0·455
1 hour	0·486
1½ hours	0·520
2 hours	0·521
3 hours	0·514

All results are the average of at least duplicate analyses.

Low results were also obtained if no addition of sodium or potassium sulphate were made to increase the boiling point of the digestion mixture. The time required for the mixture to clarify was increased from between ¾ and 1¼ hours to between 2 and 3 hours and subsequent digestion times of up to 4 hours continued to give low results (see Table 2).

TABLE 2.

Effect of Digestion with Sulphuric Acid Only.

Digestion Time After Clearing.	Observed Nitrogen Content Percentage.
2 hours	0·347
2½ hours	0·404
4 hours	0·464

All results are the average of duplicate analyses.

Shirley and Becker (6) observed that, for the determination of nitrogen in pyridine type compounds, copper sulphate was an inefficient catalyst, while mercury was satisfactory.

The catalyst used by Poth *et al.* (3) was a mixture of copper sulphate and mercuric oxide, so their individual efficiencies for the determination of nitrogen in shale oil were examined.

Analyses were run in duplicate using 0·5 gm. of the individual catalysts instead of 0·5 gm. of each with a final digestion time of two hours.

The results were:

Copper sulphate	0·508, 0·520	0·514% N.
Mercuric oxide	0·528, 0·519	0·523% N.
Mixed catalyst		0·520% N.

The differences between these duplicates were greater than customary with the mixed catalyst but were not considered significant. On the basis of this experiment, however, the use of the mixed catalyst was continued.

DISTILLATION.

In order to reduce the amount of attention required during the distillation of the ammonia several minor modifications to the customary set-up were made.

Instead of distilling through a splash trap to retain caustic spray, the ammonia-laden steam was bubbled through boiling water. A Claissen flash was substituted for the simple distillation flask recommended for this purpose by Thorpe and Whitely (7) as being more efficient.

Fitting the distillation receiver with a bunsen valve, as recommended by Meneghini (8) greatly reduced the danger of accidental " suck-backs ".

All water used for washing and dilution purposes was carefully redistilled from caustic soda and the first fractions which contained any traces of ammonia discarded. In order to reduce the possibility of contamination the ammonia-free water was stored in glass stoppered bottles and only a minimum stock kept in hand.

Absorption of the ammonia vapours in boric acid solution followed by titration of the ammonia with sulphuric acid using screened methyl red indicator gave more uniform results than absorption in sulphuric acid, followed by back titration with caustic soda solution (Table 3).

TABLE 3.

Difference between Duplicate Analyses.

Acid Used.	Difference between Duplicate Analyses.		Number of Duplicates.
	Mean.	Standard.	
Boric	0·0055% N.	0·0068% N.	60
Sulphuric	0·0132% N.	0·0193% N.	25

FINAL METHOD.

The method finally adopted is as follows: The following materials were weighed into a 500 ml. Kjeldahl digestion flask:

40±0·5 gms. sodium bisulphate.
or
30±0·5 gms. anhydrous sodium sulphate.
0·5±0·05 gms. copper sulphate.
0·5±0·05 gms. mercuric oxide.

Approximately two grammes of the crude oil were carefully weighed (to the nearest milligramme) into the digestion flask by means of a Lunge pipette. Forty ml. of concentrated sulphuric acid were added, if sodium bisulphate was used, and 50 ml. if sodium sulphate was used, and the flask rotated to mix the contents. Heating was then commenced with a small flame.

During the first part of the digestion the heating had to be carefully controlled because of the foaming tendencies of the digestion mixture. After the foaming ceased the flask was heated strongly so that sulphuric acid vapours refluxed in the bottom of the neck of the flask but did not distill off. The time at which the mixture turned clear green was noted and the digestion continued for a further two hours. After cooling till crystallization had just commenced the acid was carefully diluted with 100–120 mls. of ammonia-free distilled water. This was done carefully and with shaking to avoid layering in the flask.

This diluted acid was poured into the distilling flask and the digestion flask rinsed with a further 200 ml. of water, which were also added. Two to three grammes of granulated tin or zinc were added with two to three grammes of pure paraffin wax to reduce foaming.

One hundred millilitres of ammonia-free water were charged into the Claissen flask and 50 ml. of 4% boric acid charged into the titration flask and the apparatus connected up (Fig. 2).

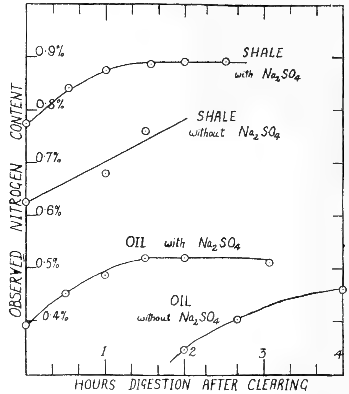

Fig. 1—Effect of Digestion Conditions on the Observed Nitrogen Content of Oil Shale & Shale Oil.

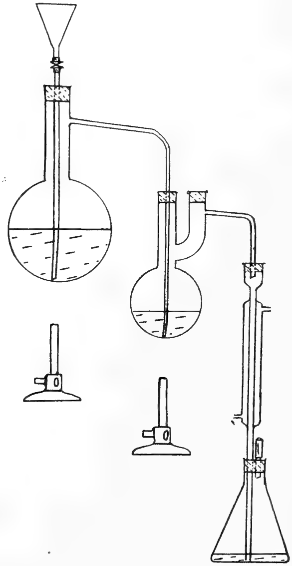

Fig. 2—Distillation Apparatus.

Ten millilitres of 25% sodium sulphite solution (to decompose mercury ammine complexes) were added to 250 mls. of 40% caustic soda solution and the mixture charged to the distillation flask through the funnel. Use of an ordinary glass funnel connected to the delivery tube by means of a length of rubber tubing which could be sealed with a screw slip was quite satisfactory and eliminated the possibility of frozen stop-cocks. After the addition of the caustic soda solution a few bubbles of air were blown through the solution to mix it. Failure to mix the acid and the caustic solution thoroughly could cause serious bumping or even priming when the distillation was started.

The distillation was commenced and the water in the Claissen flask boiled at such a rate that its volume did not change significantly during the process. When approximately 250 mls. of water had distilled into the titration flask the distillation was stopped and the condenser rinsed into the flask with approximately 20 c.c. of previously neutralized water. Four drops of the screened methyl red indicator were added and the solution titrated with decinormal sulphuric acid.

Blank determinations were carried out with a 2 g. sample of sugar or naphthalene on each lot of reagents and at frequent intervals during the process of a long series of analyses.

OIL SHALE.

After the successful application of the Kjeldahl method to shale oil the work was repeated with oil shale to see if the same or different conditions were required. It was found that the digestion proceeded more smoothly with the shale than with the oil, but otherwise the results were very similar.

The effects of the extra digestion time on the observed nitrogen content of the shale was determined and found to be the same as with the shale oil. Also, as with the oil, the addition of sodium sulphate to the digestion mixture was necessary for the complete recovery of the nitrogen present. The results are given in Table 4.

TABLE IV.

Effect of Digestion Conditions on the Observed Nitrogen Content of Oil Shale.

(*a*) Without added Sodium Sulphate.

Additional Time of Digestion.	Observed Nitrogen Content Percentage.
Nil	0·623, 0·627
1 hour	0·678, 0·683
1½ hours	0·759, 0·760

(*b*) With added Sodium Sulphate.

Additional Time of Digestion.	Observed Nitrogen Content Percentage.
Nil	0·736, 0·808
½ hour	0·835, 0·845
1 hour	0·880, 0·869
1½ hours	0·896, 0·880
2 hours	0·889, 0·895 } 0·893 av.
2½ hours	0·890, 0·899 }

DISCUSSION.

The only nitrogenous constituents of shale oil that have been identified are pyridine homologues; pyrroles are also present but no individual member of this series has yet been identified in shale oil (9). Other types of nitrogen compounds are most certainly present in the oil (10). At present practically nothing is known of the structure of the nitrogenous constituents of shale (11).

Shirley and Becker (6) found that, for the determination of nitrogen in pyridine type compounds by the Kjeldahl method, a total digestion time of three to four hours was required in order to obtain the full nitrogen value. Cole and Parks (12) found that pyridine type compounds required approximately three times as much digestion as other nitrogen compounds. In a study of the Kjeldahl determination of the nitrogen content of coal Beet and Belcher (13) isolated pyridine carboxylic acids from the products of the digestion and Beet (14) identified nicotinic acid among them. Woodward *et al.* (15) obtained yields of up to 76% of theory of nicotinic acid by the controlled Kjeldahl digestion of various β-substituted pyridine derivatives, and suggested the commercial application of the method.

These observations confirm the relatively slow oxidation of the pyridine nucleus under the conditions of the test and suggest that the analytical difficulty is a function of the high resistance of the pyridine nucleus to sulphonation. Other work at present in progress indicates that this property may allow the approximate determination of the amount of pyridine type compounds present in a material such as oil shale. On the basis of present data it is suggested that approximately 20% of the nitrogen present in the sample of shale examined is present in the form of pyridine rings.

SUMMARY.

The conditions have been determined for the accurate determination of the nitrogen content of shale oil and oil shale by the Kjeldahl method. A minimum digestion time of one and a half hours from the time the digestion mixture clears is necessary for the correct result to be obtained in both cases. This appears to be due to the presence of compounds containing pyridine nuclei.

ACKNOWLEDGEMENTS.

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NITROGEN IN OIL SHALE AND SHALE OIL.

VI. Acid Washing of Crude Shale Oil.

By Geo. E. Mapstone, M.Sc., A.A.C.I., M.Inst.Pet.

Manuscript received, June 2, 1948. Read, July 7, 1948.

Introduction.

The presence of organic nitrogen compounds has been found to have an important bearing on the behaviour of an oil towards catalytic cracking or hydrogenation. For example, Gordon (1) reports that the nitrogen content of a coal oil for hydrogenation must be kept below five parts per million in order to maintain a high activity for the tungsten sulphide hydrogenation catalyst.

Since all the nitrogen compounds that have been identified in shale oil in the past have been basic in character, the effect of an acid wash on the nitrogen content of the crude shale oil was examined to see if it could throw some light on the nature and distribution of the nitrogenous constituents of the shale oil.

Cold Sulphuric Acid Wash.

Since sulphuric acid is the cheapest commercial strong acid, it was the natural choice, and its use was examined in detail. The acid was applied in varying concentrations and amounts. When using 5% to 10% w/v. acid the aqueous acid phase separated as such from the oil with a small amount of a tar. This enabled an estimate of the volume of the extracted tar bases to be made. When 25% w/v. or stronger acid was used the acid separated from the oil as a sludge.

Experimental Procedure.

(*a*) *Washing Crude Shale Oil with 25% w/v. or Stronger Acid.*

Two hundred to 250 ml. of oil was measured into a separating funnel and the calculated amount of the sulphuric acid added. After two minutes' thorough shaking the mixture was allowed to settle for half an hour. The oil was then decanted, centrifuged and measured. Any sludge remaining in the separating funnel was drained into the centrifuge tube. With the thicker sludges this step was facilitated by warming the funnel to about 180° F. in an oven. After centrifuging the volume of sludge was measured. Traces of sludge left adhering to the separating funnel were disregarded.

With the concentrated (90%) acid a distinct temperature increase was obtained on contacting the acid and the oil. The maximum temperature increase in the acid phase was recorded, the temperature of the oil phase being approximately two degrees lower.

(*b*) *Washing Crude Shale Oil with 5% and 10% w/v. Acid.*

Cold Treatment. Two hundred to 250 ml. of oil was measured into a separating funnel and shaken for two minutes with the calculated amount of the acid. After settling for half an hour the spent acid was separated and centrifuged to remove traces of oil and tar before measurement. The washed oil was then centrifuged to remove traces of acid and tar before measurement. Tar adhering to the sides of the separating funnel was liquefied by heating in an oven at about 180° F. for 15 to 20 minutes and then poured into the centrifuge tube for measurement.

The approximate volume of tar bases extracted from the oil was determined by rendering the filtered acid extract strongly alkaline with 40% caustic soda solution in a separating funnel that did not have very much air space. The liberated tar bases were extracted with 10·0 mls. of xylene and the volume of the extract measured in a burette after settling. The increase in the volume of the xylene was taken as the volume of tar bases liberated.

The results obtained using 5%, 25%, 50%, 75% and 90·4% (commercial concentrated) w/v. sulphuric acid are presented in Tables 1 to 5.

TABLE 1.

Treatment of Crude Shale Oil with Cold 5% Sulphuric Acid.

Pounds H_2SO_4 per Bbl. Oil.*	Percentage Oil Recovered.	Sludge and Tar Percentage.	Tar Bases Percentage.	Nitrogen Content Percentage.
0	—	—	—	0·518
3	97·6	1·2	—	0·483
5	96·0	1·6	0·8	0·476
10	96·0	1·8	1·0	0·434
15	96·0	2·0	1·0	0·444
20	96·0	1·6	1·0	0·416

* 1 bbl.=35 imp. gals.

TABLE 2.

Treatment of Crude Shale Oil with Cold 25% Sulphuric Acid.

Pounds H_2SO_4 per Bbl. Oil.	Percentage Oil Recovered.	Sludge and Tar Percentage.	Nitrogen Content Percentage.
0	—	—	0·518
5	94·0	4·8	0·384
10	91·0	8·5	0·352
15	87·5	10·5	0·331

TABLE 3.

Treatment of Crude Shale Oil with Cold 50% Sulphuric Acid.

Pounds H_2SO_4 per Bbl. Oil.	Percentage Oil Recovered.	Sludge and Tar Percentage.	Nitrogen Content Percentage.
0	—	—	0·518
5	92·0	7·5	0·379
10	90·5	9·0	0·317
15	84·0	14·5	0·249

TABLE 4.

Treatment of Crude Shale Oil with Cold 75% Sulphuric Acid.

Pounds H_2SO_4 per Bbl. Oil.	Percentage Oil Recovered.	Sludge and Tar Percentage.	Nitrogen Content Percentage.
0	—	—	0·518
5	94·0	6·0	0·362
10	80·0	10·0	0·302
15	87·0	12·3	—

TABLE 5.

Treatment of Crude Shale Oil with Cold 90·4% Sulphuric Acid.

Pounds H_2SO_4 per Bbl. Oil.	Percentage Oil Recovered.	Sludge and Tar Percentage.	Temperature Rise ° C.	Nitrogen Content Percentage.	Sulphur Content Percentage.
0	—	—	0	0·518	0·66
5	91·4	9·8	6·1	0·303	0·68
10	87·2	15·2	8·9	0·156	0·78
15	82·0	20·4	10·7	0·150	0·72
20	80·4	24·0	11·2	—	0·64
25	79·2	26·0	13·8	—	0·60
30	78·0	27·2	14·0	0·104	0·59

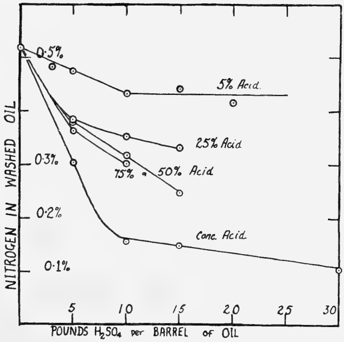

Fig.1.—Effect of H_2SO_4 Amount & Concentration on the Nitrogen Content of Crude Shale Oil.

These results indicate that at least three different classes of nitrogen compounds exist in the oil. The first class, which consists of the true tar bases and is extractable with dilute sulphuric acid, accounts for approximately 15% to 20% of the nitrogen in the oil. This small proportion of bases in the oil is in line with the observations of Bailey *et al.* (2), who found that very little of the nitrogen compounds in crude flow oils can be extracted with dilute acid.

The second class is not extractable with dilute sulphuric acid but is polymerized to give a heavy tar by the more concentrated acid, the tar being deposited as such or dissolved in the acid sludge. The 90% acid completely polymerized this class, while 5% to 10% acid had relatively little effect and the 25% to 75% acids were intermediate in effect. This second class probably consists of high molecular weight pyrroles or similar compounds which are readily polymerized by acids. It accounts for approximately 50% of the nitrogen in the oil.

The third class, which accounts for the residual 30% or so of the nitrogen in the oil, consists of non-basic, acid-stable compounds which are only sparingly soluble in the acid sludge, as shown by the slight but definite decrease in the nitrogen content of the residual oil on treatment with excess acid.

HOT SULPHURIC ACID WASH.

In a larger scale experiment to prepare a quantity of washed oil, 20 gallons of crude oil were added to a 44-gallon drum containing one gallon of concentrated sulphuric acid dissolved in 14 gallons of water. The drum was heated externally with a steam jet to reduce the viscosity of the oil for easier mixing and the acid contacted with the oil by passing a stream of compressed air through it for 12 hours. At the end of this time the oil did not discolour 5% sulphuric acid when shaken with it, so the extraction of the bases was considered to be complete.

TABLE 6.

Extraction of Bases from Crude Shale Oil.

Crude Oil—	
Total nitrogen before extraction	0·542% N.
Lab-washed with 5% H_2SO_4	0·428% N.
Drum washed with 5% H_2SO_4	0·346% N.
Sulphur content	0·56% S.
Tar Formed—	
Amount	Approx. 4%
Nitrogen content	1·94%
Sulphur content	2·82%

TABLE 7.

Treatment of Crude Shale Oil with Hot Dilute Sulphuric Acid.

Acid Strength. W/v.	Pounds H_2SO_4 per Bbl. Oil.	Treatment.	Percentage Oil Lost.	Weight Percentage Tar and Sludge.	Volume Percentage Bases.	Nitrogen Content Percentage.
—	—	Nil.	—	—	—	0·530
5%	5	Cold wash.	3½	n.d.	0·2	0·445
5%	5	Brought to boil.	1	1·15	0·2	0·408
5%	5	Boiled 5 minutes.	n.d.	1·0	0·2	0·414
5%	5	Boiled 10 minutes.	2	1·2	0·2	0·410
5%	5	Boiled 15 minutes.	3	1·25	0·25	0·426
5%	10	Cold wash.	3	n.d.	0·6	0·436
5%	10	Brought to boil.	3	1·4	0·5	0·420
5%	10	Boiled 5 minutes.	3	1·5	0·8	0·400
5%	15	Cold wash.	3	n.d.	0·5	0·420
5%	15	Brought to boil.	3	1·6	0·4	0·410
5%	15	Air passed.*	10	2·0	n.d.	0·420
10%	10	Brought to boil.	7	n.d.	0·8	0·414
25%	10	Brought to boil.	7	1·05%	0·7	0·322

* Air was passed five minutes before boiling. The oil was then brought to the boil and air passed for a further five minutes.

Examination of the treated oil (Table 6) showed that the " drum " treatment had reduced the nitrogen content by 0·196% against a reduction of 0·114% on washing with an equal volume of 5% sulphuric acid in the laboratory. Check analyses were carried out, but only confirmed these figures. On draining the drum a quantity of a heavy tar was obtained. This amounted to approximately 4% of the crude oil treated and its high nitrogen content (1·94%) accounted almost completely for the further reduction in the nitrogen content of the residual oil.

An attempt was then made on a laboratory scale to reproduce this result in the hope of finding the reason for the additional polymerization by the dilute sulphuric acid. The oil was boiled with varying amounts of acid for various lengths of time (see Table 7). This modification of the treatment was not successful though, with the boiling, as great a reduction in the nitrogen content was obtained with 5 lb. of acid per barrel of oil as with 15 lb./bbl.; whereas, in the cold, the larger amount of acid was slightly more effective. The boiling treatment caused the colour of the acid solution to become much stronger and darker than with the cold treatment.

Hot Treatment. Two hundred to 250 ml. of oil and the requisite amount of the acid were heated in a tared flask under reflux and the boiling continued for varying periods of time. When cold the volume of residual oil was measured as with the cold wash. The flask was rinsed with water, drained and allowed to dry before weighing to determine the weight of tar, all of which adhered to the glass.

It has been observed that crude shale oil deposits a solid product on atmospheric oxidation (3) and the analysis of such a deposit compares with that of the polymerization tar from the drum test, viz. deposit 2·23% N., 1·28% S.; tar, 1·94% N., 2·82% S.; crude oil 0·54% N., 0·56% S. It was therefore considered that the air used for stirring the drum could have been the active polymerizing agent. However, passing air through the boiling acid and oil in the laboratory gave no significant effect other than a somewhat greater oil loss from evaporation of the light ends in the air stream and a slightly greater tar yield (Table 7).

The use of boiling 10% sulphuric acid showed no improvement over use of the 5% acid. The nitrogen content of a sample of oil which has been brought to the boil with 25% sulphuric acid showed a significantly greater decrease. In this case two distinct tars were formed; one stayed between the oil and acid, where it gave difficulty in separation of the acid liquor, and the other (1·05%) sank below the acid.

The tar deposited in the flask in all the boiling tests was dissolved out in acetone and the solvent allowed to evaporate spontaneously. The acetone-free residue consisted of a mutually insoluble oil and tar. The oil contained 0·411% nitrogen, indicating that it was washed oil that had been entrained in the tar deposit. The tar contained 2·62% nitrogen, which suggests that the lower molecular weight compounds are the more readily polymerizable of the class and thus give rise to a greater nitrogen content of the tar.

OTHER ACIDS.

McKee and Parker (4) recommend the use of 25% acetic acid rather than dilute mineral acids for the removal of bases from oils. The effect of an acetic acid wash on the nitrogen content of crude shale oil was therefore examined. The acid concentration had relatively little effect on the results (Table 8), the residual nitrogen content remaining relatively constant with treatment with 10 pounds or more of acetic acid per barrel of oil. The acid and oil broke cleanly and there was no sign of tar formation with oil temperature below approximately 150° F.

TABLE 8.

Treatment of Crude Shale Oil with Dilute Acetic Acid.

Pounds Anhydrous Acetic Acid per Bbl. Oil.	Acid Concentration.		
	5% Acid Nitrogen Content Percentage.	10% Acid Nitrogen Content Percentage.	25% Acid Nitrogen Content Percentage.
Nil..	0·621	0·621	0·621
3 lb.	0·597	0·608	0·600
6 lb.	0·557	0·558	0·562
10 lb.	0·564	0·583	0·574
15 lb.	0·576	0·578	0·573

TABLE 9.

Treatment of Crude Shale Oil with Dilute Acids (Two Volumes of Acid Used to One Volume of Oil).

Acid Used.	Acid Strength.	Nitrogen Content Percentage.	Nitrogen Decreased Percentage.	Remarks.
None.	—	0·609	—	
Acetic.	25%	0·529	0·080	No tar formed.
H_2SO_4.	1·0 N.	0·500	0·109	Some tar formed.
HCl.	1·0 N.	0·419	0·190	Appreciable tar.
HNO_3.	1·0 N.	0·360	0·249	Large amount of tar.

Further tests were carried out to check the action of various acids on the removal of nitrogen from crude shale oil. It was found that the acids examined could be placed in the following order of increasing activity : acetic, sulphuric, hydrochloric and nitric acid (Table 9). The nitrogen-removing activity of the acids was paralleled by their tar-forming activity, acetic acid giving no tar and nitric acid giving a large amount. Accurate measurement of the tar formed was not practicable, so only the qualitative result was recorded, as this was quite satisfactory for purposes of comparison.

It is suspected that the greater polymerizing activity exhibited by the nitric acid may have been due, at least in part, to its oxidizing power, though this would not be great in the normal solution used. The use of this acid, however, failed to achieve even a 50% reduction in the nitrogen content of the oil.

DISTRIBUTION OF NITROGEN IN OIL.

A sample of crude shale oil that had been carefully vacuum fractionated (1 mm. mercury abs.) in connection with some other work was examined. The nitrogen content of the various fractions was determined both before and after washing with 5% sulphuric acid. Unfortunately insufficient sample was available for the cuts to be washed with concentrated acid as well.

The results (Table 10) show that both the total and the non-basic nitrogen compounds increase with the boiling point of the fraction. The basic or extractable nitrogen content increases to a maximum in the 500–600° F. cut and then falls steadily. It is interesting to note that less than half the nitrogen content of the fraction boiling in the gasoline range (to 360° F.) is sufficiently basic to be extracted with 5% sulphuric acid. Unfortunately insufficient amounts of the samples (only 5 to 20 c.c.) were available to determine the loss of oil on washing with the acid. Also the original oil and the distillation bottoms had been discarded and so could not be examined for their nitrogen content. However, the nitrogen content of the original oil could be taken as approximately 0·57% by analogy with similar samples. Since 0·32% of nitrogen (based on the total oil) has been accounted for in the oil distillate, 0·25% has to be accounted for in the distillation residue, which would therefore contain 2%.

TABLE 10.
Nitrogen Content of Crude Oil Fractions.

Boiling Range.	Fraction in Cut.	S.G. at 60° F.	Nitrogen Content.		
			Total.	After Acid Wash.	Decrease.
To 360° F.	14·2%	0·758	0·106	0·058	0·048
360–500° F.	9·9%	0·812	0·152	0·071	0·081
500–600° F.	13·0%	0·849	0·276	0·100	0·176
600–700° F.	13·5%	0·879	0·414	0·246	0·168
700–800° F.	18·1%	0·903	0·580	0·432	0·148
800–900° F.	18·7%	0·926	0·708	0·579	0·129
Bottoms	12·6%	(By difference)			

Nitrogen content of distillate on basis of original crude oil—	
Total nitrogen	0·321%
Nitrogen after acid wash	0·223%
Decrease	0·098%
Nitrogen content of original oil	0·57% (est.)
Approximate nitrogen content of residue	2·0% (est.)

Horne, Finley and Hopkins (5) observed the decomposition of secondary amines from shale oil to give ammonia and tertiary amines on distillation, but the evolution of ammonia was not observed during the distillation of this oil. The bases extracted from the crude oil fractions by dilute sulphuric acid account for 0·098% of nitrogen in the original sample. This is of the same order as the amount removed from the unwashed oil by the same treatment. Therefore, unless, as seems most unlikely, the distillation residue contained a very high proportion of tar bases, it appears that the use of the high vacuum successfully inhibited this decomposition of the secondary amines.

EFFECT OF THERMAL CRACKING ON THE NITROGEN IN THE OIL.

The nitrogen content of various fractions of products from the Dubbs thermal cracking point was then investigated in order to determine the effect of thermal cracking on the nitrogen in the oil. In a parallel with the observations on the crude oil the nitrogen content of the fractions increased with the boiling point of the fractions, the residuum and coke containing over 1% of nitrogen (Table 11).

TABLE 11.

Nitrogen Content of Dubbs' Fractions.

	Total Nitrogen.	Nitrogen after Acid Wash.	Percentage of Contained Nitrogen Soluble in Acid.
Typical crude oil charge ..	0·52%	0·42%	19
Heavy recycle oil ..	0·684%	0·375%	45
Light recycle oil	0·470%	0·103%	78
Cracked naphtha	0·283%	0·048%	83
Residuum	1·042%	—	—
Coke—			
8·25% V.M. ..	1·502%	—	—
1·0% V.M.	1·033%	—	—

Residuum contained 1·04% nitrogen and a sample of coke that had been strongly heated in the laboratory until the volatile matter content had been reduced to 1% contained only 1·03% nitrogen, whereas a sample of normal coke containing 8·25% volatile matter contained 1·50% nitrogen. This indicates that a large proportion of the nitrogen in the crude shale oil, probably that observed to remain in the bottoms on vacuum distillation, accumulates in the residuum. On cracking to coke this nitrogen remains behind in the coke with normal operation but, should the coking conditions be intensified part of it is then split off.

The fraction of the total nitrogen content of the different cuts that could be extracted with 5% sulphuric acid decreased with increase in the boiling point of the cut but was, in all cases, much higher than in the raw crude oil. This indicates that the " non-basic " nitrogen compounds in the crude had probably been, at least partly, converted to true tar bases under the cracking conditions. This effect is parallel to the observations of Bailey *et al.* (2) on the conversion of the initially non-basic nitrogen compounds in crude flow oil to tar bases on cracking.

The presence of relatively large amounts of ammonia and traces of hydrogen cyanide in the cracked gases (6) indicate that appreciable and far-reaching decomposition of some of the nitrogen compounds had taken place.

OTHER OILS.

Some samples of shale oil produced in different manners were examined. These samples included oils produced from different shales on a commercial scale by various firms, and oils produced from Glen Davis shale in various manners. A sample of flow oil from Lakes Entrance (Victoria) was also examined and is included for comparison.

The results presented in Table 12 show that the range of the nitrogen contents of oil from Glen Davis shale is much smaller than the total range observed with the oils from various sources. At the same time a much larger proportion of the nitrogen from the other shale oils is acid-soluble. This applies to the oil from the N.T.U. retorts of Lithgow Oil Pty. Ltd., which have been claimed to give less cracked oils than the Fell retorts as used by National Oil Pty. Ltd. If this is so factors other than the thermal history of the oil are important in determining the nature of the nitrogen compounds in the shale oil.

TABLE 12.

Nitrogen Content of Shale Oils from Various Sources.

Producer.	Shale Source.	Nitrogen Content Percentage.		Remarks.
		Total.	Acid Washed.*	
Lithgow Oil Pty. Ltd.	Marangaroo.	0·792	0·486	Very little tar.
Mudgee Motor Fuels.	Peter's Creek.	0·810	0·547	Very little tar.
	Peter's Creek.	0·168	—	
Lewgil Oil Co.	Torbane.	0·627	0·398	Approx. 10% tar and sludge.
N.O.P. (No. 1 Bench).	Glen Davis.	0·518	0·42	Tables I and V.
N.O.P. (No. 2 Bench).	Glen Davis.	0·609	0·500	Table IX.
N.O.P. Grey King Assay.	Glen Davis Retortables.	0·549	—	—
N.O.P. Grey King Assay.	Glen Davis Main Seam.	0·603	—	—
		0·526	0·406	—
Benzol extract of Main Seam shale.	Glen Davis.	0·600	—	—
Lakes Entrance, Victoria.	Flow oil.	0·094	0·069	—

* Washed once with an equal volume of cold 5% sulphuric acid and centrifuged to remove suspended acid.

DISCUSSION.

The nitrogen compounds present in crude shale oil fall into three classes. The first class consists of basic nitrogen compounds which may be extracted with dilute acids. These bases are probably all pyridine type bases such as have been isolated from shale oils by several workers. Quinoline homologues may be present, though none have been identified with certainty in shale oils and they may be considered as pyridine type bases for the present.

The second class consists of the dilute-acid-insoluble nitrogen compounds which are polymerized by strong acids. This description tallies with the properties of the pyrroles which are very feebly basic and are readily polymerized in the presence of strong acids. Pyrroles have been detected as a class in shale oils by several workers, but no individual member of the series has, as yet, been isolated and identified. The degree of substitution of the pyrrole nucleus affects the stability towards acids, and this fact could readily explain the different degree of polymerization by the different acids and different acid concentrations. The possibility that other types of nitrogen compounds may be present here must not, however, be overlooked.

The third class of nitrogen compounds is stable to concentrated sulphuric acid and is not appreciably extracted by it, though some partition between the oil and acid appears to take place. Possible types of nitrogen compounds that could be expected to have these properties are the oxazoles, diazines, carbazole, etc. It is not considered likely that di- or triphenyl-amines, which would give comparable reactions, would be present in the crude shale oil, though the presence of the heterocyclic nitrogen compounds with two or more hetero atoms in the molecule are considered as likely to be present.

The increased proportion of the nitrogen that is present as tar bases in the partially cracked oils is in agreement with Bailey's observations (5) with flow oil that the non-basic nitrogen compounds give rise to tar bases on cracking.

The oil from the N.T.U. retort is normally considered to have been subjected to less secondary cracking than the oil from the Fell or other retorts. The higher proportion of tar bases in this oil either confutes this or some other factor must be operating. This other factor may well be that the much higher temperature reached in the combustion zone in the N.T.U. retort, which is above the oil distillation zone, decomposes to tar bases some of the nitrogeneous materials in the shale residue which is passed out as such from the Fell retort. This suggestion is supported by the fact that approximately 50% of the nitrogen originally present in the kerogen is left in this shale residue. If this does happen both the total nitrogen and the tar base content of the oil would be increased by these additional bases.

SUMMARY.

The nitrogen compounds in crude shale oil have been shown to fall into the three classes :

(1) Tar bases, which may be extracted by dilute acid.
(2) Dilute-acid-insoluble but acid-polymerizable compounds.
(3) Compounds stable towards and not extractable by concentrated sulphuric acid.

Twenty-five per cent. acetic acid will extract the tar bases without significantly affecting the second class, while dilute (normal) mineral acids cause some polymerization of the second class at the same time.

The total nitrogen content of the crude shale oil increases with the boiling point. The tar bases increase to a maximum (% N.) in the 500–600° F. fraction and then decrease again but, even with the gasoline fraction, they contain but part of the total nitrogen present in the fraction.

On thermal cracking the fraction of the nitrogen in various cuts appearing as tar bases increases. A large proportion of the nitrogen in the oil remains in the residuum and coke. The nitrogen content of shale oils from several different sources has been examined.

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NITROGEN IN OIL SHALE AND SHALE OIL.

VII. Distribution of Kerogen Nitrogen on Carbonization.

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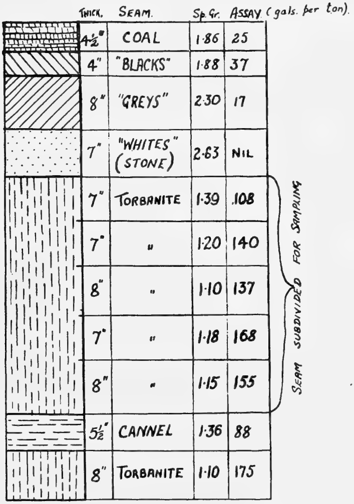
Introduction.

In order to obtain further background information regarding the nitrogen in oil shale and shale oil the distribution of the nitrogen of the kerogen on carbonization was examined.

Firstly it is necessary to describe the shale seam itself. The shale mined at Glen Davis comes from two composite seams which are mined and retorted together. The accompanying figure gives a detailed cross-section of the seam. Both the relative thickness and richness of the various portions of the seam vary throughout the deposit, but the various bands retain their identity throughout the deposit.

Glen Davis Shale Seam.



Thick.	Seam.	Sp. Gr.	Assay (gals. per ton).
4½"	COAL	1·86	25
4"	"BLACKS"	1·88	37
8"	"GREYS"	2·30	17
7"	"WHITES" (STONE)	2·63	NIL
7"	TORBANITE	1·39	108
7"	"	1·20	140
8"	"	1·10	137
7"	"	1·18	168
8"	"	1·15	155
5½"	CANNEL	1·36	88
8"	TORBANITE	1·10	175

Sample Nos. M294-M305.

TABLE 1.

Examination of Shale.

	Main Seam.		Secondary Seam.		
	Torbanite.	Cannel.	" Blacks."	" Greys."	Coal.
Proximate analysis of dry shale—					
Volatile matter ..	49·0%	43·2%	22·4%	18·0%	19·8%
Fixed carbon ..	18·1	27·0	7·0	1·0	26·8
Ash	32·9	29·8	70·6	81·0	53·4
V.M./F.C. ratio ..	2·7	1·6	3·2	18·0	0·74
Kerogen content of shale (*a*)	67·1	70·2	29·4	19·0	46·6
Kerogen content of shale (*b*)	—	68·8	24·9	12·0	43·6
Distribution of products on carbonization—					
Crude oil percentage by weight ..	54·0	23·2	10·5	2·8	7·7
Coke percentage by weight	40·75	72·5	75·1	86·1	83·9
Water distillate percentage by weight	6·25	1·5	4·5	7·0	3·0
Ammonia plus loss percentage by weight		1·8	9·9	9·9	5·4
Ash content of coke percentage by weight	56·5	47·2	88·9	93·9	58·9
Organic content of coke percentage by weight	43·5	52·8	11·1	6·1	41·1

(*a*) Assuming shale=kerogen+ash. This does not allow for the presence of the inorganic " retained " water in the shale, which is therefore reported as kerogen here.

(*b*) Assuming shale=kerogen+ash+" retained " water. The water obtained on retorting is here assumed to all be " retained " water which is also not strictly correct.

WORK DONE.

Samples of the different types of constituents of the shale seam were examined to determine the amount of nitrogen present and its distribution on carbonization.

The torbanite and the cannel were carbonized in the Gray King furnace to 600° C., while the blacks, greys and coal were carbonized to 600° C. in a one pound retort in order to obtain sufficient oil for testing. The yields of the various products of carbonization are recorded as percentages by weight of the charge. The samples were also characterized by proximate analysis (Table 1).

The distribution of the kerogen of each sample on carbonization was calculated from the nitrogen content of the raw shale, the coke and the crude oil. The analyses were carried out by the method previously described (2). No attempt was made to determine the amount of ammonia formed during carbonization so it is included with that small amount of the nitrogen liberated as elemental gas as " ammonia plus loss ". The results of the nitrogen distribution are given in Table 2.

The oils were washed with an excess of 5% sulphuric acid and the nitrogen content of both the washed and unwashed oils determined. There was insufficient of the samples for the volume of bases extracted to be determined. However, the decrease in the nitrogen content of the oil after washing could be taken as a measure of the amount of tar bases formed. The acid wash of the oils from the

TABLE 2.

Nitrogen in Shale.

	Main Seam.		Secondary Seam.		
	Torbanite.	Cannel.	"Blacks."	"Greys."	Coal.
Nitrogen contents percentage by weight—					
Shale	0·726	1·080	0·254	0·080	0·945
Coke	0·920	1·330	0·198	0·070	0·986
Crude oil	0·526	0·662	0·616	0·554	0·924
Crude oil after washing with 5% sulphuric acid	0·406	0·461	0·456	0·381	0·386
Tar	—	—	Formed	—	1·245
Kerogen	0·96	1·53	0·86	0·89	2·03
Organic ash-free coke	2·12	2·56	1·79	1·15	2·40
Distribution of nitrogen on carbonization—					
Percentage in residue	51·5	89·3	58·8	75·0	87·5
Percentage in crude oil	39·0	14·2	25·6	1·9	7·5
Percentage in ammonia and loss	9·5	3·5	15·6	23·1	5·0
Percentage as tar bases	8·8	4·7	6·7	0·6	?
Percentage as non-basic compounds in oil	30·2	9·5	18·9	1·3	1·9 Tar* 6·1
Percentage extractable nitrogen in oil	25·0	31·0	35·0	32·0	—

* Assuming oil gave 40% of tar on washing with acid.

main seam shale, the cannel and the "greys" gave slight traces of tar and quite an appreciable amount of tar was formed from the oil from the "blacks". The oil from the coal gave approximately 40% by volume of a fairly hard tar, sufficient of which was available for its nitrogen content to be determined. As with the acid polymerization tars from the crude shale oil, the nitrogen content of the tar was higher than that of the oil (1).

DISCUSSION OF RESULTS.

It will be noted that the V.M. : F.C. ratio of the cannel is intermediate between those of the coal and of the torbanite and other portions of the seam.

This confirms the previous classification given to the various sections of the seam. The abnormally high V.M. : F.C. ratio of the "greys" is due to the large amount of water which is retained and chemically bound by the mineral constituents of the shale, being recorded as "volatile matter" in the test.

For the purposes of reporting the nitrogen contents of the kerogen the shale has been assumed to consist only of ash and kerogen. This is not strictly correct as the ash obtained by burning off the kerogen is not the same as the mineral matter in the shale. The inorganic minerals in shale are frequently hydrated and do not lose the water of hydration by heating just to 105° C. On ignition this water is given off and thus changes the composition of the inorganic constituents of the shale; this is particularly so in the "greys". In connection with this point carbonates such as calcium carbonate liberate carbon dioxide on ignition if present and thus decrease the ash content of the original inorganic matter in the shale. Fortunately there is little if any carbonate in the Glen Davis shale.

The organic constituents of the shale or kerogen also tend to give some water of decomposition on carbonization, so it is not correct to take the water condensed in the carbonization assay as inorganic " retained " water, though it probably comes mainly from this source. The kerogen contents of the shales have been calculated on both of these bases for comparison (Table 1) but the nitrogen content (Table 2) has been based on the initial assumption that the shale consists of ash and kerogen only.

The calculated nitrogen contents of the kerogens on this basis are most interesting. The kerogens of the main seam, torbanite the " blacks " and the " greys " have approximately the same nitrogen content (0·96%, 0·86%, 0·89% respectively), while the cannel (1·53%) is intermediate between the shales and the coal (2·03%).

The nature of the organic precursors will naturally influence the final nitrogen content of the different sections of the deposit.

Since the nitrogenous materials concentrate during the formation of coal (3), difference in the nitrogen contents could possibly be taken as indicating that the shales have not been so fundamentally changed on " maturing " or weathering as the coal, and that the cannel has " matured " to an intermediate extent.

In each case over half the nitrogen of the kerogen remains in the coke.

It will be noted that the nitrogen contents of the ash-free portion of the coke of the blacks and greys are lower than for the other parts of the seam. These two samples also produced the highest proportions of water on carbonization. These two factors may well be connected as numerous workers have shown that the admission of steam to the carbonizing shale increases the yield of ammonia at the expense of the nitrogen content of the shale coke (e.g. 4, 5, 6, 7, 8). Unfortunately no explanation is available for the 103·5% recovery of the nitrogen in the cannel coal. The analyses were made in duplicate and the duplicates checked well.

The high percentage of the nitrogen from the " blacks " and the " greys " appearing as ammonia and loss may possibly be due to the factor mentioned previously, that the " retained " water converted some of the coke nitrogen to ammonia during the carbonization, though it would be expected that this effect would be slight.

On acid washing the oil from the coal, the acid was discoloured, showing the presence of tar bases. However, the oil gave a large amount of tar amounting to approximately 40% by volume. Using this figure with the respective nitrogen contents of the washed oil and tar accounts for 8·0% of the nitrogen of the shale as against 7·5% accounted for in the unwashed oil. This correlation is not the best but is as good as can be hoped for with the small samples available for examination.

With the other four oils the tar bases account for from 25% to 35% of the nitrogen in the oil. These figures are a little higher than those obtained earlier with commercially produced crude shale oil (1), but it will be noted that the nitrogen reduction by the acid wash was greater with the sample that gave the greatest amount of tar of the four. It is therefore likely that tar formation may be the explanation of the somewhat greater reductions obtained here.

For purposes of comparison the results of some other workers on the distribution of the nitrogen of shale on carbonization are given in Table 3 together with the results obtained in this work.

TABLE 3.
Distribution of Nitrogen.

Shale.	Reference.	Percentage Nitrogen Distributed in			Loss.
		Coke.	Oil.	Ammonia.	
Scottish	8	62·6	20·4	17·0	—
Scottish, distilled very slowly	8	45·7	20·0	32·8	1·5
American, in stream of hydrogen	6	21·0	24·9	49·0	5·1
Weimarn (U.S.S.R.) ..	7	—	—	5·5	—
Volga (U.S.S.R.) ..	7	—	—	18·9	—
Glen Davis—					
Torbanite	—	51·5	39·0	9·5	Ammonia plus loss for the Glen Davis samples.
Cannel	—	89·3	14·2	—	
" Blacks "	—	58·8	25·6	15·6	
" Greys "	—	75·0	1·9	23·1	
Coal	—	87·5	7·5	5·0	

SUMMARY.

Samples of shale from different parts of the Glen Davis seam have been examined and the distribution of the nitrogen on carbonization determined. Over half the nitrogen originally present in the shale remains in the carbonization residue.

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THE LATE PRECAMBRIAN ICE-AGE AND GLACIAL RECORD OF THE BIBLIANDO DOME.*

By DOUGLAS MAWSON.

With Plates X-XIII and three text-figures.

CONTENTS.

In doing honour to a pioneer of Australian geology on the occasion of this Clarke Memorial Lecture, I shall deal with a phase of geological enquiry not appreciated and explored in his day. At that time, geologists were already well acquainted with rôle of ice as a geological agent in eroding the face of the earth and in the accumulation in moraines of characteristic deposits resulting from such erosion. The key to the interpretation of such-like phenomena was furnished by the study of existing glaciers. It was later a comparatively simple matter to apply knowledge so gained to the elucidation of the record of the Pleistocene Ice-Age.

Then followed discovery of the evidence of extensive glaciation in late Palæozoic time. In this connection it is interesting to note that the first evidence of this ice-age discovered in this continent was made in South Australia by A. R. C. Selwyn in the year 1859. Later, in 1877, there followed Professor Ralph Tate's observation in the Hallett Cove area. This thoroughly aroused the interest of Australian geologists in locating further evidence of long past glaciations, and led to discoveries evidencing late Palæozoic glaciation, widely spread in Australia as well as elsewhere in the world.

Stimulated by these discoveries, geologists in South Australia eventually found evidence of a still more ancient glaciation, the first accepted record of Precambrian age. In this case the suggestion first came from H. P. Woodward in 1889, when accounting for a remarkable boulder rock met with near the northern end of the Flinders Ranges. Later, convincing proof of the existence of tillite in South Australian late Precambrian or early Cambrian strata was forthcoming in the year 1901 as a result of the field activities of Walter Howchin.

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* The Clarke Memorial Lecture delivered to the Royal Society of New South Wales, July 15, 1948.

During the past 45 years, records of glaciation in past ages and distributed through many geological periods have come from all quarters of the earth. Apart from such as relate to the present Pleistocene-Recent Ice-Age, these testimonies of severe refrigeration are grouped in time, mainly about the closing stages of the Palæozoic era on the one hand and of the Precambrian on the other. It is now well established that in the Late Carboniferous and during much of Permian time, possibly extending over a period of 10 to 20 million years, our world lived through a glacial epoch greater in magnitude than that so far experienced in the present glaciation which, after all, has been in existence for a mere million years or so. Here in Australia evidences of late Palæozoic glaciation have been mounting up, until now sufficient to demonstrate that certain areas of this continent then supported ice-caps of great magnitude.

Still more remarkable is that, during the past 50 years, evidence of widespread glaciation in late Precambrian and eo-Cambrian times has been accumulating to such a degree that there can no longer be any doubt but that at that time, also, the world was in the throes of a severe ice-age. Evidence now forthcoming in South Australia, as a result of an extended study of the sedimentary record of that period, leaves no doubt as to the existence then of a vast land ice-cap in southern Australia, extending through a considerable period of time. The evidence for this conclusion is the main subject of my thesis this evening.

HISTORICAL.

Throughout a period of some 30 years, following upon his original demonstration of the existence of tillite interbedded among the more ancient strata of South Australia, Howchin continued to contribute accounts concerning the nature and extent of still further outcrops of this tillite which he designated the Sturtian Tillite, since it was first encountered by him in the gorge of the Sturt Creek near Adelaide. A list of such contributions appears in the bibliography incorporated herewith. During this long period Howchin traced the extension of this tillite over a very wide area in South Australia, a region some 400 miles in extreme length by 150 miles in extreme width.

This area was extended further to the east into western New South Wales by the author in 1906, firstly to Olary then to the Barrier Ranges, across the border (Mawson, 1909). Later, Jack (1915) reported what is apparently a reappearance of this tillite far to the north-west in the Everard Ranges. Subsequently, further details of occurrences within this area have been published by various authors. Mention of such is incorporated in the bibliography appended hereto.

At an early stage of investigation of the tillite and associated beds at Olary and in the Barrier Ranges, the author was convinced that the sedimentary record of this ancient glaciation is more complex, and extended through a longer period of time than indicated in Howchin's publications. Evidence of repeated advance and withdrawal of the ice was noted, and the glacio-fluvial origin of associated sediments was recognized. Thus in a contribution entitled " Extra-Glacial Sedimentation " read by me before the Association for the Advancement of Science in January, 1907, it was argued that the banded shales overlying the tillite at the Sturt Gorge and that of a lower horizon at Glen Osmond, both near Adelaide, was of glacio-fluvial origin. That contribution was in the nature of a discussion on the probable character of fluvial sediments deposited during an ice-age beyond the limits of the wholly glacial. In the views then advanced, I was assisted by an account of laminated glacio-lacustrine clays in Michigan by Berkey (1905) and by correspondence with Professor T. C. Chamberlin of Chicago, but, at that time, was unaware of the great work of Baron de Geer then in progress in Scandinavia. On that occasion, in illustration of the principles laid down, it was held that on the basis of their petrological character, a considerable thickness of beds underlying the Sturtian tillite in the region of Adelaide, as far down as the laminated slates below the arkosic quartzite of Glen Osmond, were products of the ice-age period, thus advocating the earlier appearance of glacial conditions than that proved by the Sturt Gorge tillite itself. It was contended that the discovery elsewhere in South Australia of a tillite contemporaneous with the Glen Osmond beds might well be expected: the latter being regarded as the glacio-fluvial equivalent, beyond the actual limits of the ice. Publication of this paper was held over to permit of further elaboration and documentation. In search of first-hand knowledge of the conditions of sedimentation during an ice-age, it was then that the author welcomed an invitation to join an expedition (Shackleton's) proceeding to Antarctica.

It is obvious that little if any record of a great ice-age may ultimately be preserved on an elevated land surface subject to severe ice-cap glaciation. The complete historical document recording events during the progress of an ice-age can be preserved only in deep basins adjacent to elevated crustal blocks subjected to glaciation. In such places opportunity may be offered for the accumulation of an unbroken sequence of deposits embodying the complete story of the period represented.

Fortunately we have in South Australia an extensive geosynclinal basin whose initiation long preceded the oncoming of the late Proterozoic ice-age and which continued to receive sediments for a long period subsequent to its passing. Here, then, we have conditions most favourable for the study of sedimentation during the passage of that ice-age. In due course, it was discovered that the glacigene sediments available for study in South Australia are much more complete than is offered in Antarctica, where the products of glacial erosion are almost entirely dumped on the floor of the surrounding ocean and thus not available for investigation.

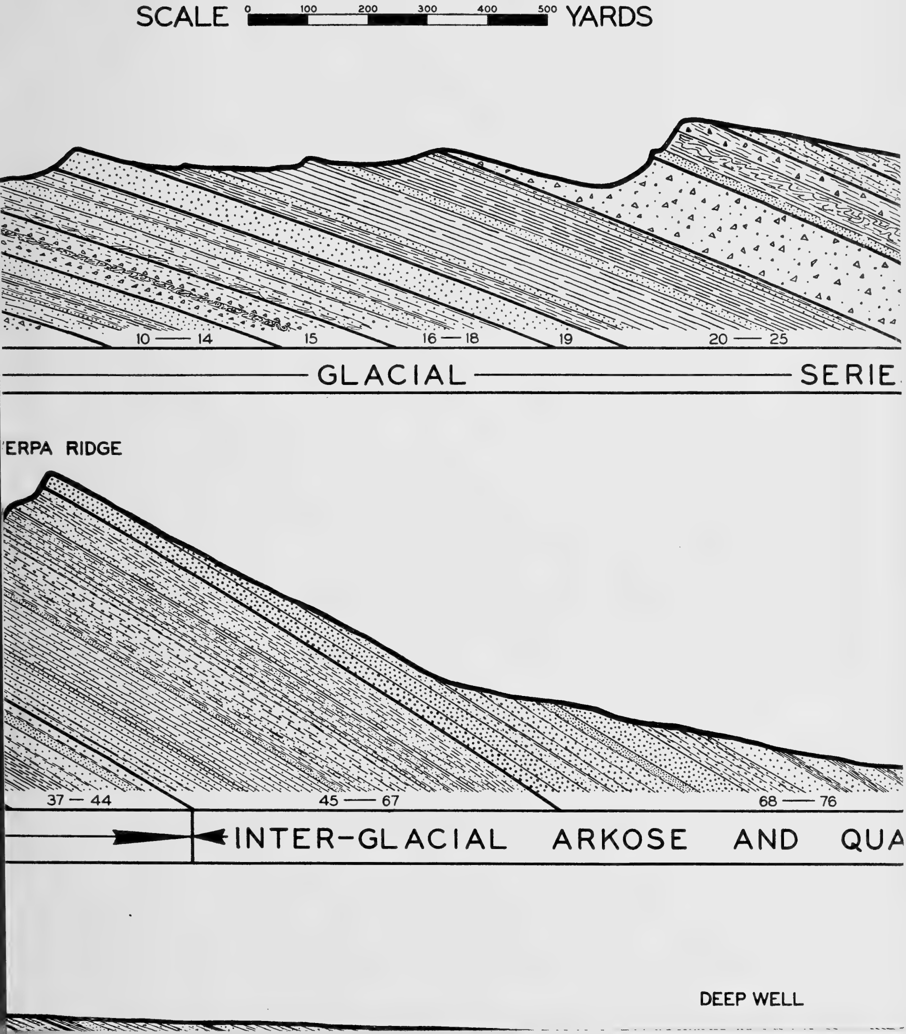
As opportunity offered during very many years past, observations concerning these ancient glacigene sediments of South Australia have been made until eventually, in 1939, the author succeeded in locating in the Bibliando Dome a long-sought opportunity to study an unusually complete and fully extended record of the sediments of that time. This investigation was completed in 1942 and has vindicated the views advanced in 1907 as stated above.

This great and deeply eroded structure, displaying an enormous thickness of strata, was located when investigating the more central area of the geosynclinal basin. The heart of the domed region is occupied by Bibliando Sheep Station; accordingly it is referred to as the Bibliando Dome. In it is exposed the most complete section of the glacigene beds of the South Australian late Proterozoic succession yet encountered. In view of the great importance of this record to a discussion of the glaciation evidenced at that period and, further, in consideration of the value of such to the study of glacigene sediments of a great ice-age, I am furnishing herewith a more than usually detailed account of the succession there exposed.

The Bibliando Dome.

The topographical relief exhibited in the Flinders Ranges is primarily the result of differential erosion of the mass of sediments originally deposited in the Proterozoic-Cambrian geosyncline and later elevated as a folded mountain chain, the result of a Middle- to Late-Cambrian orogeny (Mawson, 1942, 1947). Subsequent peneplanation was followed by block elevation, apparently coinciding with the Kosciuskan period (Middle-Pliocene into Pleistocene) of displacements, which raised the region high above the surrounding peneplaned lowlands and permitted the inauguration of the present cycle of erosion which, in its turn, has

THWARDS FROM CENTRE OF DOME — BI



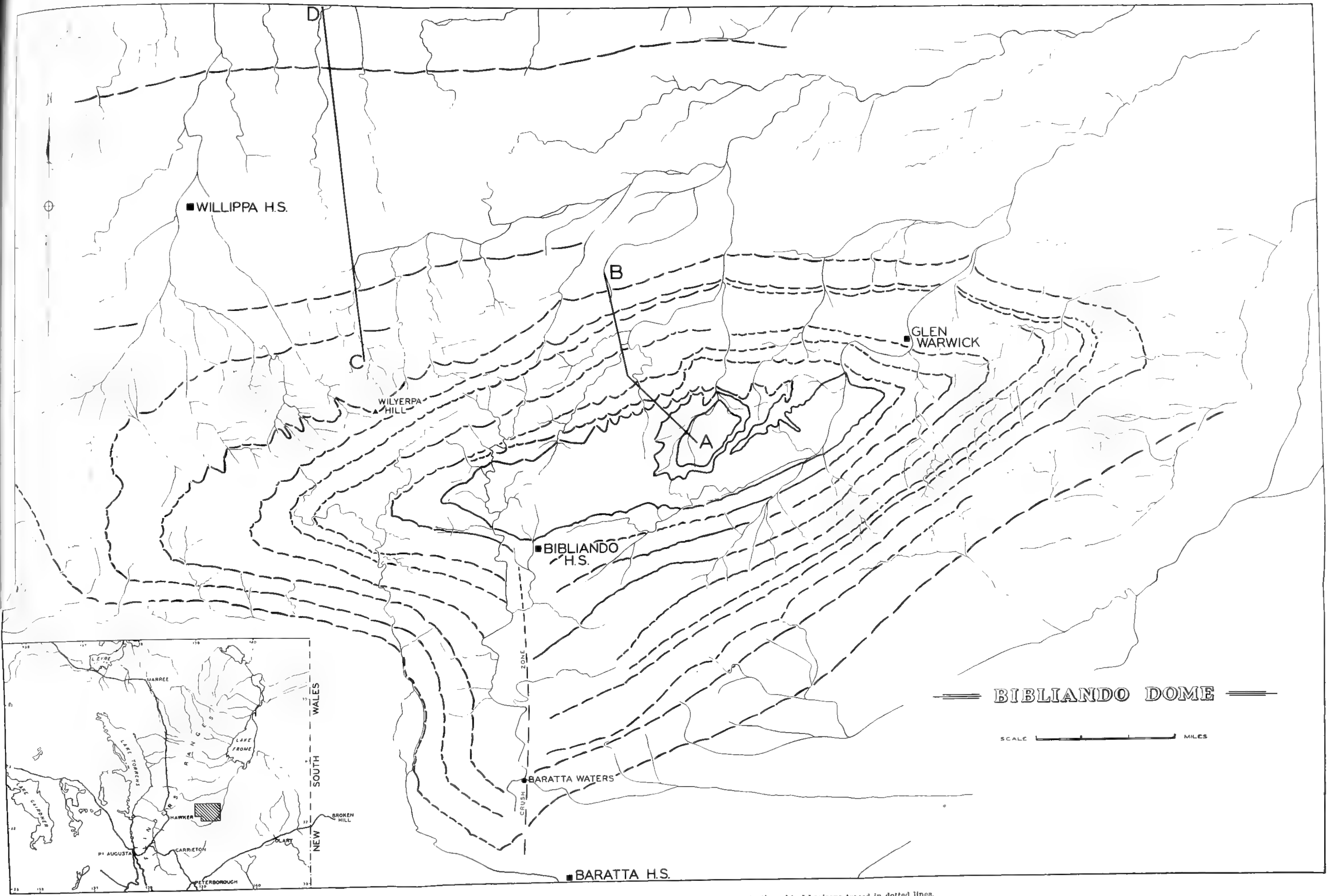


Fig. 1.—Plan of the Bibliando Dome illustrating structure. Outcrop of leading stratigraphical horizons traced in dotted lines.

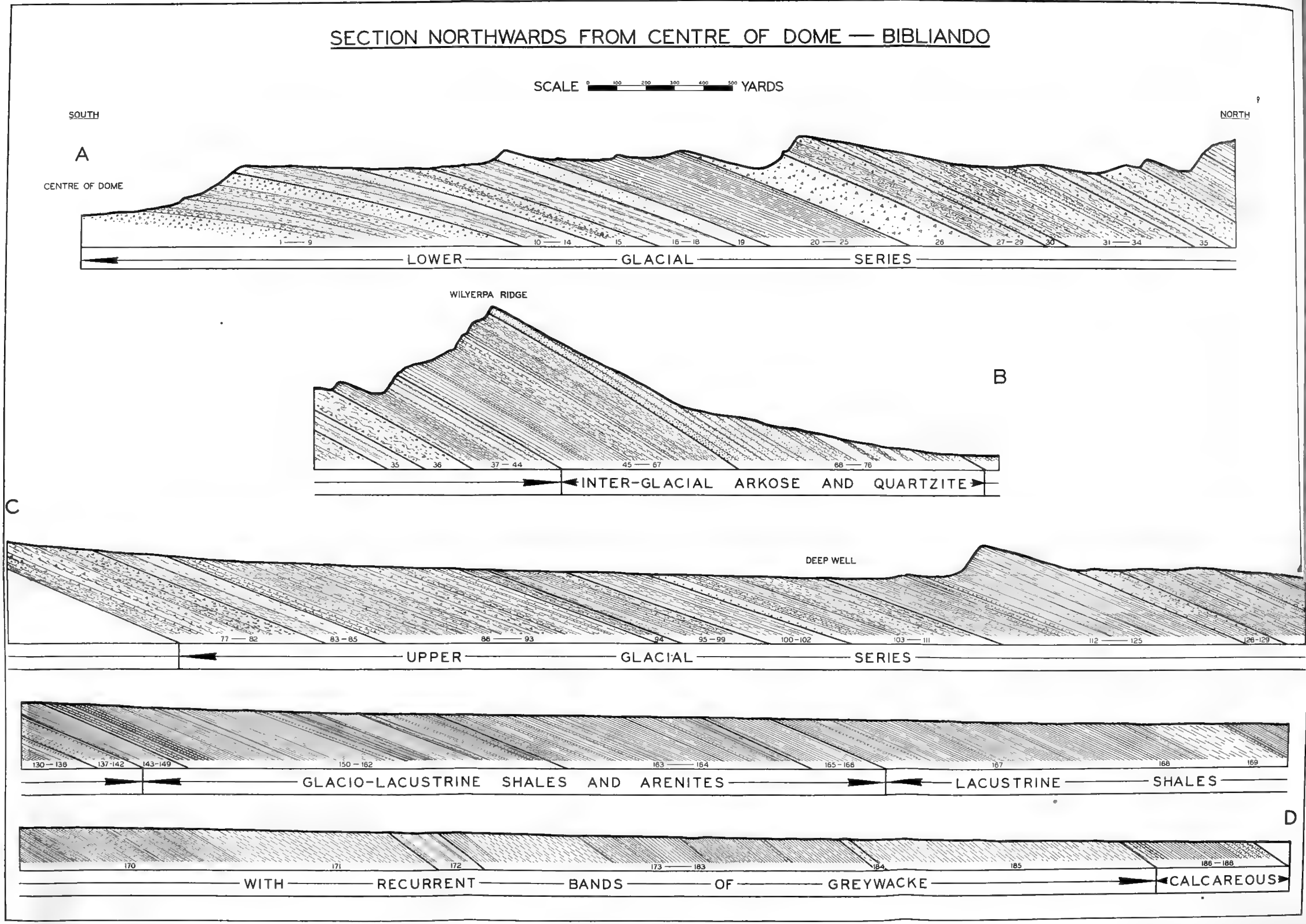
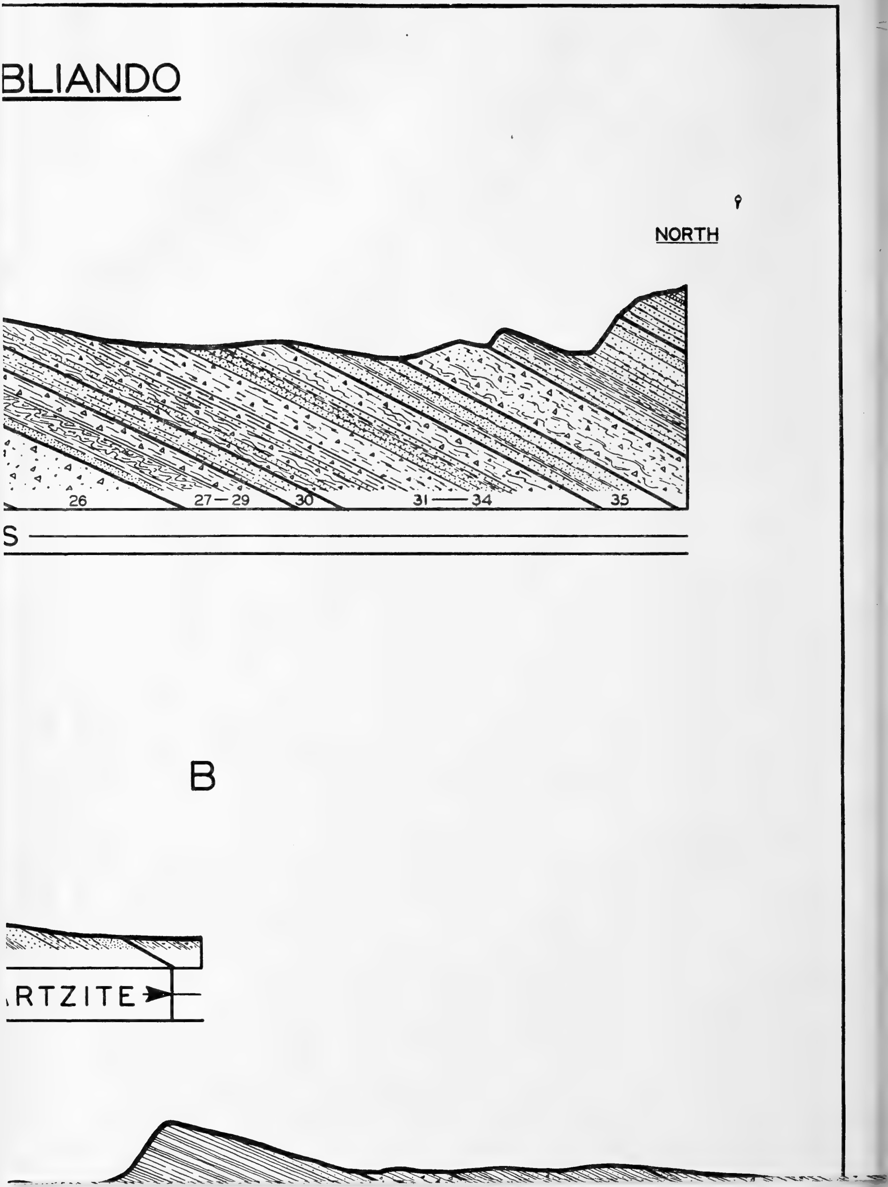


Fig. 2.—Sequence of Strata of the Bibliando Dome.


BLIANDO
NORTH
26
27—29
30
31—34
35
S
B
RTZITE

accounted for the existing very striking topographic relief. Basins and domes are well exemplified in the structures illustrated. Of the former, Wilpena Pound is an outstanding example. Of the latter none is more perfect than the Bibliando Dome.

On page 153 is a plan of the Dome as plotted from aerial photographs of the region supplied by the Royal Australian Air Force. Scrutiny of the aerial photographs confirmed our ground reconnaissance in its finding of absence of faulting and serious distortion of the strata along the lines selected for geological section. However, the aerial photographs reveal notable disturbance of the strata immediately beyond the northern limit of our section.

Plate X is a vertical aerial photograph over part of the Bibliando Dome in the neighbourhood of Wilyerpa trigonometrical station (indicated by a white cross) and Bibliando Homestead (indicated by a white circular spot). This view illustrates the rugged nature of the country.

The centre of the Dome is situated approximately on a line joining Hawker and Silverton, about 42 miles east of Hawker and 58 miles north-north-west of Yunta. Willippa sheep station lies to the north of it ; to the south is Baratta sheep station. Between the two is a high elevated region defined by a thick series of interglacial quartzites and arkoses encircling a central region occupied by soft, glacigene sediments. Viewed from afar (Plate XI, Fig. 1) this great quartzite range with its remarkably accordant summit level limned against the sky is a really striking feature. Viewed from above, the elevated ring of quartzite surrounding the hollowed-out core region gives the impression of a gigantic crater. This latter is breached in three places by outflowing streams. One has broken through the southern wall along a crush zone, the result of faulting. Two others, travelling respectively in a north-easterly and easterly direction, break through the quartzite wall in its weakest section. Recently a homestead has been established within the crater pound, with access by way of the bed of the stream leading south through the shatter zone towards Baratta Station.

The highest point of the quartzite rim is known as Wilyerpa, but at a distance its superior elevation is scarcely noticeable. Wilyerpa rises to about 3,040 feet above sea-level. The lowest part of the pound floor is about 1,290 feet below the summit of the high ridge line. The low country encircling the elevated ring of quartzites, located some 1,600 or 1,700 feet below the highest point of the quartzite ridge, is occupied by a second great series of comparatively easily eroded glacigene sediments leading on to lacustrine shales and limestones.

Plate XI, Fig. 2 is a view from just below Wilyerpa trigonometrical station, showing some of the periclinal quartzite ridges which constitute the elevated rim surrounding the central erosion basin—a domed pound.

The appearance of portion of the descent into the pound on the north side is illustrated in Plate XII, Fig. 1. There the strata inclines to the north at an average dip of about 28 degrees. A view across the centre of the Dome where the strata are horizontally disposed is illustrated in Plate XII, Fig. 2.

Details of a geological section extending northward across the strata of the Dome are tabulated below and further illustrated in graphic form against the surface relief in the folded page 154 herewith, where they are plotted approximately to scale.

It will be observed that this section was run in two divisions. The lower section from the centre of the dome to item 76 inclusive was measured along the line A-B as indicated in the folding map, on page 153. At B the line of section arrives at a flat alluviated region ; consequently, in order to examine and record the upward extension of strata the line of section was then transferred to a hilly, well relieved belt of country some five miles to the west. There the sequence of beds recorded as items 77 to 188 inclusive was observed along the line C-D.

This line of section passes through Deep Well, a convenient camping centre where abundance of water is available. From Deep Well, Wilyerpa summit can be easily reached by an ascent of about 1,590 feet.

The stratigraphical succession listed herewith is set out in numerical order from below upwards, beginning in tillite in the centre of the Dome. The thickness of each of the recordings is the true thickness stated in feet. Bearings, where mentioned, are true, not magnetic. Names applied to sediments take consideration of their original unmetamorphosed form: thus such terms as shale and sandstone will be used notwithstanding that they may be in the state of slate or quartzite.

It is unfortunate that the Dome is not more deeply dissected and so permit the section to be extended completely through the entire record of that glacial epoch. However, as several boulders of magnesite were found in the creek bed downstream from this locality, originating in all probability as erratics in the tillite, it is likely that the section begins close to the base of the glacial series, for we have, in localities further to the west, for example at Mundallio Creek, observed magnesite erratics from the underlying formation in the basal portion of the tillite.

COMPLETE RECORD OF STRATA OF THE BIBLIANDO DOME.

(Stated in Ascending Order.)

Section along the line A-B.

		Feet
1.	Grey, tillite with a large proportion of aqueo-glacial, rock-flour: containing erratics (granite, quartzite, gneiss), etc., up to 2 ft. diam. Horizontal to a 4° dip to the north	67
2.	Tillite; near the base contains large erratics (to 30 ins.) but, above, only smaller boulders	26
3.	Glacio-lacustrine rock-flour and silt rock with occasional bands of glacial grit	27
4.	Outcrop obscured. Probably a soft rock-flour rock	57
5.	A steep face of sandstone; soft and silty below to hard and laminated above	30
6.	Glacio-lacustrine rock-flour rock with large erratics (to 15 ins.), the latter usually confined to certain horizons. Dip 4°	42
7.	Glacio-lacustrine, rock-flour rock with a zone about 20 ft. in thickness, of large erratics (schist, quartzite, granite, red porphyry) commencing about 95 ft. from base of this item. The largest erratic observed was granite, measuring 6 ft. by 4 ft. ..	125
8.	Sandstone. Strike N. 63° E.	3
9.	Glacio-lacustrine, rock-flour rock with large erratics (granite, porphyry, quartzite, tourmaline, pegmatite, mica schist, chiastolite schist) to 2 ft. diameter. A notable sandstone dyke cuts this section. Dip 10°	135
10.	Glacio-lacustrine, silty to sandy rock-flour rock. No erratics observed	79
11.	Laminated, quartz-rich arenite	2
12.	Rock-flour rock with some zones notably sandy	70
13.	Outcrop largely obscured by alluvium. The non-resistant underlying rock is probably sandy shale	23
14.	Sandstone	86
15.	Glacio-lacustrine, rock-flour rock with several horizons rich in erratics. One granite erratic 4 ft. diam. Intraformational puckering observed. Strike N. 64° E., dip 15°	190

		Feet
16.	Glacio-lacustrine, rock-flour rock with occasional sandy horizons of from a few inches to several feet in thickness. The lower limit is a laminated arenite with intraformational puckering	115
17.	Sandstone	14
18.	Rock-flour rock with arenaceous horizons. Slightly undulating. Dip 16°	146
19.	Sandstone, especially hard at the base. Forms a ridge on the landscape	130
20.	Rock-flour rock	75
21.	Sandstone	15
22.	Rock-flour rock	216
23.	Sandstone	6
24.	No observable outcrop. Apparently soft rock-flour rock	158
25.	Rock-flour rock with interbedded arenaceous bands	63
26.	A rock-flour rock with conchoidal fracture embedded in which at intervals are erratics (mica-schist and granite)	352
27.	Sandstone	30
28.	Rock-flour rock with some arenaceous horizons which vary in thickness from a few inches to several feet as a maximum. No erratics observed. The arenaceous horizons frequently exhibit bedding planes and contortions	136
29.	Glacio-lacustrine, rock-flour rock with sandy horizons. Embedded are occasional mica-schist and granite erratics. Strike N. 70° E. Dip 20°. Outcrops along the top of a ridge	91
30.	Sandstones and greywacke alternating with rock-flour silts	98
31.	Chiefly rock-flour silty shales; minor interbedded sandstone horizons. Some small erratics and puckering	224
32.	Chiefly silty, rock-flour shales with some erratics and puckering	140
33.	Mainly arenites. Some interbedded silts and mudstones	117
34.	Glacio-lacustrine, rock-flour bed; laminated and puckered in places. Occasional erratics	126
35.	Dominantly arenaceous sandstones, siltstones and greywackes. Dip 24°	182
36.	Mainly glacio-lacustrine, rock-flour shales with occasional erratics; puckering noted	252
37.	Soft arenaceous and silty beds	85
38.	Rock-flour rock with sandy bands more abundant near the base	20
39.	Rock-flour rock for the most part exhibiting claystone fracture; sandy bands are rare	50
40.	Alternating beds of rock-flour rock and arenite (the section here crosses a major creek)	64
41.	Mainly hard sandstone but with some interbedded greywacke and rock-flour claystone. Dip 25°	130
42.	Resistant sandstone	34
43.	Sandy bands alternating with fine greywacke	20
44.	Shaley glacial greywacke. Erratics appear at 30 ft. above the base of this section	44
45.	Resistant sandstone	32
46.	Soft sandstone	40
47.	Resistant sandstone	12
48.	Soft sandstone	60
49.	Resistant sandstone	14
50.	Soft sandstone	30
51.	Sandstone	21

		Feet
52.	Sandy shale	128
53.	Somewhat resistant arenaceous formation	11
54.	Soft beds obscured by alluvium	41
55.	Alternating sandstone and sandy shale. Sandstone beds each about 2 ft. thick	63
56.	Sandy shale and some sandstone bars	35
57.	Resistant quartzite. Dip 30°	20
58.	Sandy shale	35
59.	Quartzite	3
60.	Fluvio-glacial claystone	15
61.	Hard quartzite	8
62.	Siltstone and shale with infrequent bands of sandstone	109
63.	Resistant sandstone	5
64.	Soft shaly beds	19
65.	Soft sandy shale and sandstone covered by talus	68
66.	Largely obscured by talus. Mainly slaty claystone and shale	45
67.	Sandstone with surface covered by talus rubble	40
68.	Quartzite. Outcropping on the ridge is a bold, almost vertical face. Strike N. 75° E., dip 31°	50
69.	Mainly massive quartzite, but there are some thin silt bands in upper 20 ft. Normal bedding planes and current bedding are discernible though poorly marked	70
70.	Gritty arkosic sandstone with some angular pebbles near the base but passing upwards into sandstone and siltstone, the latter increasing towards the top	60
71.	Mainly sandstone and quartzite partly arkosic and siltstone intercalations in very minor amount	211
72.	Strong quartzite, arkosic in part	119
73.	Siltstone and felspathic grit	132
74.	Mainly quartzite, felspathic in places, in four divisions separated by minor developments of softer siltstone and some felspathic grit	376
75.	Less resistant siltstone and grit	64
76.	Siltstones and sandstone terminated above by a belt of hard quartzite	126

Section along the line B-C.

77.	Laminated silt rock with occasional pebble bands; the latter more abundant near the top, where there is also a bed of sandstone 4 ft. thick. Strike N. 76° E., dip 25° to north	155
78.	Flaggy to massive glacio-fluvial silts and sands more arenaceous near the base. Occasional pebble beds in which one quartzite erratic measured 18 ins. diameter	171
79.	Glacial mudstones with some embedded erratics; less arenaceous in upper section	30
80.	Somewhat arenaceous, laminated, glacio-lacustrine rock-flour flags with some grit bands	24
81.	Arkosic sandstone with large erratics to 9 ins. diameter	3
82.	Glacio-lacustrine mudstones to rock-flour flags with occasional bands of pebbles. Some contorted and swirl bedding observed. Strike N. 66° E., dip 24°	110
83.	Unsorted glacio-lacustrine mudstone. No erratics noted	114
84.	Rather arenaceous, glacio-lacustrine mudstone. No erratics observed	70

		Feet
85.	Glacio-lacustrine mudstone and siltstone with only slight indication of lamination	39
86.	Glacio-fluvial sandstone and siltstone with recurrent pebble bands	93
87.	Resistant arkosic sandstone	10
88.	Laminated, silty rock-flour beds with some grit bands	140
89.	Laminated and flaggy aqueo-glacial rock-flour rock; also siltstone and mudstone with some grit and small pebble bands	160
90.	Laminated, rock-flour flags and siltstone with small-scale ($\frac{1}{2}$ in. to 12 ins. banding). Occasional bands contain small pebbles	101
91.	Sandy and shaly glacio-lacustrine beds with occasional bands of unsorted glacial mud in which grit and some small erratics occur	232
92.	Glacio-lacustrine siltstone in which are occasional pebble bands suggesting concentration by current action. Dip 21°	57
93.	Sandy mudstones with occasional bands of grit and pebbles	179
94.	Banded, glacio-lacustrine mudstone and siliceous flags	84
95.	Flaggy shales with grit bands	11
96.	Tillite with medium sized erratics	16
97.	Flaggy sandstone and grit beds	16
98.	Sandy and slaty flags with some grit and occasional pebbles	149
99.	Flaggy siltstones and sandstones with occasional small pebbles. Dip 20°	65
100.	Gritty sandstone	41
101.	Rock-flour flags and glacio-lacustrine unsorted muds	87
102.	Flaggy grits and sandstones	123
103.	Flaggy, glacio-lacustrine grits. Mainly fine-grained but frequent bands of coarse grit. Occasional large erratics	33
104.	Coarse glacio-fluvial sandstone and grits	41
105.	Finer grained, glacio-fluvial grits with interbedded horizons of tillite	103
106.	Banded fine-grained, gritty sandstone	87
107.	At the base, alternating glacial muds and gravels. Above, broader bands of coarser materials and some large erratics. Strike N. 85° E., dip 20°	154
108.	Alternating flaggy glacio-fluvial, dense siltstones and grits	36
109.	Flaggy, glacio-lacustrine muds and silts	20
110.	Flaggy, glacio-fluvial, dense siltstones and sandstones	22
111.	Glacio-lacustrine mudstones with occasional laminated bands. Also some bands each only a few inches thick of unsorted tillite	40
112.	Flaggy sandstone and mudstone	20
113.	Alternating mudstones, grit and shales. Here have arrived at deep well. Dip 22°	37
114.	Sandstone	10
115.	Outcrops obscured by river flat alluvium. Probably soft, laminated, fluvio-glacial shales	144
116.	Varved shales exhibiting current wash in places. Alternating glacio-lacustrine grit and rock-flour. In this belt only occasional outcrops appear above the alluvium	215
117.	Thin flaggy shale with occasional grit bands	77
118.	Thin flaggy shale, fissile in part. Strike N. 77° E., dip 24°	114
119.	Glacio-lacustrine shale, much of which is non-laminated	100
120.	Flaggy glacio-lacustrine shale. Alternating bands of laminated and non-laminated rock-flour shale	146
121.	Dense laminated shale	67
122.	Resistant arenaceous shale	6

		Feet
123.	Glacio-lacustrine grit and shale	28
124.	Glacio-lacustrine sandstone	32
125.	Glacio-lacustrine sandstone and mudstone	11
126.	Shaly tillite with small erratics	34
127.	Arenaceous glacial mud rock	60
128.	Glacio-lacustrine grit and some erratic-bearing bands	68
129.	Tillite	3
130.	Flaggy slates	182
131.	Glacio-lacustrine mud rock	11
132.	Sandy glacio-lacustrine mud	18
133.	Glacio-lacustrine mud	41
134.	Dense, somewhat arenaceous shale	49
135.	Shales more arenaceous below	46
136.	Erratics in a sandy glacial mudstone	40
137.	Dense somewhat arenaceous shale	38
138.	Dense slates noticeable gritty below	42
139.	Dense slates	69
140.	Slate with a band of sandstone at the base	9
141.	Slate with sandstone band at base	14
142.	Tillite. Erratics of limestone and quartz	13
143.	Slate	20
144.	Slate with a 2 ft. thick band of sandstone at base	27
145.	Slate with a 1 ft. thick band of sandstone at base	38
146.	Slate with a 6 ft. thick band of sandstone at base	24
147.	Shale with a 9 in. band of gritty sandstone at base	29
148.	Shale with an 18 in. band of fine-grained arenite at base	29
149.	Shale with a 12 in. grit band at base	12
150.	Shale slightly calcareous at several horizons and a black grit band at base	73
151.	Shales, faintly calcareous at certain horizons	115
152.	Dense shales	105
153.	Shale with some lamination. At base is a somewhat arenaceous band 12 ins. thick	143
154.	Laminated shales. Strike N. 76° E., dip 19°	343
155.	Flaggy shales with somewhat calcareous bands about 12 ins. thick recurring at the following intervals recorded stratigraphically upwards from the base: at the base, at 25 ft., 32 ft., 45 ft., 64 ft., 97 ft.	105
156.	Moderately laminated, flaggy shale capped by a 6 ins. band of a bluish somewhat calcareous phase	20
157.	Well laminated shale	65
158.	Non-laminated flaggy shale suggesting original aqueo-glacial mud	15
159.	Poorly laminated shale	140
160.	Flaggy laminated shale	11
161.	Non-laminated flaggy shale, suggesting original aqueo-glacial mud	28
162.	Poorly laminated shale, with bands of a calcareous phase at the following intervals from the base of the section: 6 in. band at 66 ft., 19 in. band at 144 ft., 12 in. band at 164 ft.	233
163.	Well laminated shale with a 4 in. band of a calcareous phase at the base and an 8 in. band at 35 ft. above the base	85

		Feet
164.	Laminated shales resembling the well-known occurrence at Tapley Hill (near Adelaide) but varying in degree of obvious lamination. At some horizons this shale is slightly calcareous. More notably calcareous bands were observed at the following intervals from the base up: 4 ins. thick at base, 15 ins. at 85 ft., 6 ins. at 120 ft., 15 ins. at 173 ft., 6 ins. at 240 ft., and 9 ins. at 725 ft.	905
165.	Flaggy mudstone	23
166.	Poorly laminated, flaggy somewhat calcareous shales with a notably calcareous band 9 ins. thick at the top	268
167.	Flaggy, notably laminated, grey to blue-grey shales with interbedded bands of arenite (greywacke-sandstone) at the following intervals stated from below up: 4 ins. thick at base, 9 ins. at 104 ft., 9 ins. at 161 ft., 12 ins. at 538 ft., 6 ins. at 827 ft.	1,071
168.	Poorly laminated shales with bands of greywacke at the following intervals stated from below up: 12 ins. at 286 ft., 36 ins. at 426 ft., and 18 ins. at the upper limit	471
169.	Irregularly cleaving, somewhat calcareous slates. Dip 31°	384
170.	Somewhat flaggy laminated shales with bands of greywacke at the following intervals stated from below up: 18 ins. at the base, 6 ins. at 39 ft., 12 ins. at 117 ft., 3 ins. at 167 ft., 3 ins. at 214 ft., 12 ins. at 271 ft., 3 ins. at 334 ft., 3 ins. at 357 ft., 9 ins. at 377 ft., 6 ins. at 387 ft., 3 ins. at 394 ft., 6 ins. at 398 ft., 18 ins. at 418 ft., 9 ins. at 474 ft., 12 ins. at 495 ft., 18 ins. at 533 ft., 12 ins. at 555 ft., 24 ins. at 564 ft., 18 ins. at 608 ft., 12 ins. at 612 ft., 6 ins. at 624 ft., 12 ins. at 647 ft., 18 ins. at 670 ft., 9 ins. at 688 ft., 6 ins. at 711 ft., 3 ins. at 735 ft., 6 ins. at 750 ft., 6 ins. at 784 ft., 6 ins. at 825 ft., 18 ins. at 859 ft., 6 ins. at 887 ft., 3 ins. at 906 ft., 6 ins. at 953 ft., 6 ins. at 977 ft., 12 ins. at 983 ft., 12 ins. at 1,001 ft., 6 ins. at 1,040 ft., 6 ins. at 1,092 ft., 6 ins. at 1,123 ft., 6 ins. at 1,150 ft., 6 ins. at top	1,167
171.	Flaggy laminated grey shales	1,109
172.	Greywacke with minor grey shale bands	302
173.	Grey shales, very poorly laminated	138
174.	Greywacke	5
175.	Grey shale, very poorly laminated or without obvious lamination	706
176.	Greywacke	3
177.	Grey shales and silty shales with some laminations	327
178.	Resistant arenaceous shales	287
179.	Grey slates partly laminated	345
180.	Silty greywacke	12
181.	Grey shales in part laminated	157
182.	Greywacke	4
183.	Grey shales. A 6 in. band at 100 ft. from base is calcareous	475
184.	Resistant fine-grained greywacke	67
185.	Grey shale and slate laminated in part only. A portion of this section exhibits slaty cleavage	1,733
186.	Soft sandstone and sandy shales	139
187.	Non-resistant beds under an alluviated area. Probably calcareous shale and limestone	438
188.	Blue pisolitic limestone with bands of intraformational breccia. This corresponds to the Brighton limestone horizon of the Adelaide region	212
	Total thickness of Sediment	23,125

Summarised Statement of Strata: Bibliando Dome.

This remarkably thick series of sediments aggregating in all some 22,877 feet can be summarised by convenient assembly in cognate groups as set out below in descending order.

Calcareous, Lacustrine Shallow Water Deposits (Brighton Horizon): 789 Feet.

Item		Feet
188.	Blue pisolitic limestone with bands of intraformational breccia	212
187-186.	Sandy and calcareous shales and some sandstone	577

Lacustrine Shales with Recurrent Bands of Greywacke: 8,763 Feet.

185.	Grey lacustrine shales	1,733
184.	Fine-grained greywacke	67
183-173.	Shale, silty-shale and rare thin bands of greywacke	2,459
172.	Greywacke with minor shale bands	302
171-167.	Flaggy, laminated shales with recurrent thin bands of arenite	4,202

Glacio-Lacustrine Shales and Minor Arenites: 2,856 Feet.

166-165.	Flaggy, poorly laminated shale and mudstone	291
164-163.	Laminated shales with some narrow calcareous horizons	990
162-150.	Shale exhibiting varying degrees of lamination. Arenaceous intercalations on a very minor scale appear in the lower horizons, but are absent above where, however, slightly calcareous horizons make their appearance	1,396
149-143.	Alternating beds of glacio-lacustrine sandstone and shale	179

The Upper Glacial Series: 4,556 Feet.

142.	Tillite with erratics of limestone and quartz	13
141-137.	Glacio-lacustrine sands and shales	172
136.	Erratics in sandy mudstone	40
135-130.	Glacio-lacustrine muds and sands	347
129-126.	Shaly tillite and glacio-lacustrine grit and mud with small erratics	165
125-112.	Glacio-lacustrine, flaggy banded and varved shales, siltstones, sandstones and grits	1,007
111-103.	Flaggy glacio-lacustrine and glacio-fluvial series of mudstones, siltstones, sandstones, grits and pebble bands; with occasional thin bands of unsorted tillite	536
102-100.	Flaggy glacio-lacustrine grits, sandstones and silts. No erratics observed	251
99-97.	Flaggy glacio-lacustrine siltstone and sandstone with occasional small erratics	230
96.	Tillite with medium sized erratics	16
95-94.	Banded glacio-lacustrine muds, silts and sands	95
93-86.	Glacio-lacustrine and glacio-fluvial muds and silts with recurrent bands of grit and small erratics	972
85-83.	Glacio-lacustrine muds and silts. No erratics observed	223
82-77.	Glacial and glacio-lacustrine beds with erratics	493

Inter-glacial Arkose and Quartzites: 2,062 Feet.

76-68.	Resistant arkoses and quartzites with some minor silty partings	1,208
67-45.	Glacio-fluvial sediments, mainly arenites with some minor silty and shaly bands	854

The Lower Glacial Series : 4,095 *Feet plus.*

		Feet
44.	Glacio-fluvial silts and sands with erratics	44
43-37.	Glacio-fluvial beds, sandstones, siltstones and shales ..	403
36.	Glacio-lacustrine rock-flour shales with occasional erratics ..	252
35.	Glacio-fluvial arenites, no erratics	182
34-31.	Glacio-lacustrine beds with occasional erratics	607
30.	Glacio-lacustrine arenites alternating with rock-flour silts ..	98
29.	Glacio-lacustrine rock-flour silts with erratics and some bedded sandy horizons	91
28.	Glacio-lacustrine beds. No erratics observed	136
27.	Glacio-fluvial sandstone	30
26.	Glacial rock-flour rock with erratics	352
25-20.	Glacio-lacustrine alternating beds of rock-flour silts and sandstone	533
19.	Glacio-fluvial sandstone	130
18-16.	Glacio-lacustrine rock-flour silts with minor bands of arenite..	275
15.	Tillite with erratics	190
14-10.	Glacio-lacustrine shales, silts and sandstone. No erratics observed	260
9-1.	Tillite and glacio-lacustrine rock-flour rocks with erratics ..	512
	Total thickness exposed for observation	23,125

WARCOWIE-WILLIPPA ROAD SECTION.

At this stage it is appropriate to record that, at a point on the Warcowie-Willippa road 20 miles to the west of Deep Well, a further detailed section was run across the strike of portion of this same rock sequence.

The following is a highly summarised result giving only the thickness of the several main groups listed from above downwards :

	Feet
Pisolitic and sandy limestone (Brighton horizon)	—
Laminated shales and calcareous shale and impure limestone..	1,688
Shales, laminated and unlaminated and minor arenite ..	3,341
Upper glacial beds and glacio-lacustrine shales	8,306
Inter-glacial quartzites	—
Total	13,335

This Warcowie-Willippa road section is actually a continuation of that already published (Mawson, 1941, p. 299) extending south from the Druid Range. Item (5), the pisolitic limestone of that section, corresponds to item (188) of the Bibliando Dome section, as stated in this paper ; it is also the ceiling below which the Warcowie-Willippa road section was measured.

In this more westerly line of section several disturbances (and possibly some faulting) were encountered at a stage shortly beneath the Brighton limestone horizon. Consequently the total of 13,335 feet is possibly an understatement of the true thickness. This thickness of strata located between the Brighton limestone horizon above and the great interglacial quartzite below is to be compared with the 16,752 feet of equivalent strata recorded in the Wilyerpa section. This is a decrease to the west of over 3,000 feet. Some increase in the more easterly locality is to be expected, since it is more central in the geosynclinal trough. However, obvious disturbance and faulting in the Warcowie section may account for at least some of the deficiency.

LITHOLOGY.

The range of glacigene sediments represented in this record offers good opportunity for petrological studies. This phase of the investigation will, however, be reserved for another occasion. Attention will now be given only to some of the broader features.

In the case of the true tillites of this area, which are erratic-bearing rocks in which there is little if any evidence of bedding and where there is no evidence of sorting, the large proportion of fine rock-flour relatively to contained erratics is a notable feature. In all cases the rock-flour is coloured some shade of grey.

A number of erratics exhibiting faceting and glacial striæ were met with. Some thus striated were found actually embedded in the matrix. Except in the earlier deposits of the lower division of glacigene sediments, their average size as met with here is less than in the case in some other localities that have come under observation in South Australia.

Of the more common rock types represented among the erratics may be mentioned granite, quartzite and various schists. They include both granite and chiastolite schist corresponding so closely with similar rocks occurring *in situ* in the older Precambrian complex of the Olary-Outalpa region some 90 miles to the east as to provide convincing evidence of glacial transport from that direction.

Some horizons of otherwise normal tillite exhibit unmistakable evidence of deposition in water, in the nature of more or less well-defined bedding planes. In such cases accumulation may have taken place either in a lake or in the sea, the erratics having been transported by floating ice.

A not infrequent type of deposit is that where evidence of bedding planes is either meagre or wanting, and where the substance of the rock may be likened to a mud. Erratics are absent. In the field, I have regularly employed for such the awkward term "mother-of-till". This term was suggested, for we found that the appearance of such in the series invariably heralded the proximity of tillite.

In several locations, but more particularly interbedded with the tillites of the lower glacial series, there are formations of excessively fine and even grain-size, suggesting an æolian origin. It is difficult to account otherwise for the physical nature of these rocks. A glacio-æolian origin is more likely, as at times there is discernible no trace of bedding. In order to account for the characters exhibited in certain types of this kind of rock, I have been considering æolian transportation with final deposition in water.

A large proportion of the glacigene beds possess a marked flaggy or laminated character. Where they are of pebbles, coarse gravel or grit alternating with bands of sand, silt or rock-flour, they have been interpreted as glacio-fluvial deposits. In these the banding is on a coarse scale, usually bands several inches to a foot in thickness.

At other times the alternations are of finer grained materials, such as bands of splintery sand alternating with silt or rock-flour. Such deposits are often of the true varve type and have been interpreted as glacio-lacustrine. Splendid examples of true varving are met among these ancient glacigene sediments (Plate XIII, Fig. 1).

The coarse banded glacio-fluvial sediments are always closely associated in the series with true tillites. More remote from the tillites, the banding exhibited gradually passes into fine ribbon-like lamination so well exemplified by the Tapley Hill shale of the Adelaide region. The laminæ in the case of shale of this nature commonly range from 1/8 to 1/12 inch in thickness. Their relation to seasonal deposition is still a matter for discussion, though as already stated it was advocated by the author as such as early as 1907. These finely laminated silts and argillites are apparently the expression of peri-glacial deeper water depositions.

Shallow water peri-glacial sediments are of an arenaceous nature in which the grains are notably angular even to the extent of being splintery. When deposition has proceeded contemporaneously with adjacent glaciation these arenites are characteristically either of the arkose or greywacke type. Where deposition has proceeded at a time or place more remote from active glaciation the resultant rock approximates more and more to the character of normal sandstone.

Finally, a noteworthy feature frequently evidenced in these glacigene beds is that of intra-formational disturbances of bedding (Plate XIII, Fig. 2). Crumpling and buckling of this kind are a frequent feature of the mud and silt rocks ; occasionally they have been noted in the arenites. Among such features observed in our traverse of the Bibliando Dome some are of the nature of simple slump structures.

Lenses of fluvial sands are met with in certain of the tillite horizons. These which may be limited to a few yards in width and a few hundred yards in length appear to have originated as eskers.

The occurrence of one or more sandstone dykes up to four feet in width have been observed discordantly intersecting the glacio-lacustrine beds overlying the main tillite horizon of the lower glacial series.

Advance and Retreat of the Ice Front.

The record of strata constituting the Bibliando Dome reveals the fluctuating character of sediments deposited in that area. Variation in the nature of the depositions must have been dependent upon several changing factors, more especially linked with (1) the advance and retreat of the ice front, (2) with periodic subsidences and elevation of the land in relation to sea or lake level, (3) the shallowing or deepening of the lake or sea in which some of the deposits were accumulated.

During the progress of the ice-age certain events with far-reaching concern to the progress of sedimentation must have operated : such as (*a*) isostatic movements of the land due to ice loading and unloading, and (*b*) eustatic fall and rise of the surface of the oceans following upon ice accumulation and dissipation.

Detailed reconstruction of the climatic and geographical history of the time, based on the changing character of the deposits at any one place, is, in view of the diverse factors influencing their nature, a most uncertain problem. However, the varying degree of glacial intensity recorded in the stratigraphical succession clearly indicates that there must have been frequent notable advances and recessions of the ice front, and this on a scale suggestive of inter-glacial periods.

Formations containing erratics, and therefore depositions at a time of notable ice activity, alternate with beds free from any convincing evidence of ice transport. It will be observed that these latter are, in a number of cases, each of such thickness as to represent deposits accumulated over a period of time of considerable magnitude, corresponding to the interglacial intervals of the Pleistocene. However, it is my view that until detailed corroborative observations are accumulated from many localities scattered throughout a wide geographical area, it would be rash to place reliance on the apparent climatic significance of such features appearing in this individual record.

There can be no doubt, however, that the thick arenaceous belt represented by items (45) to (76) inclusive were accumulated during a major interglacial epoch. This accords with observations made at a number of localities in South Australia. Two such widely separated horizons of late Proterozoic tillite were met by me (as yet unpublished data) in the Olary district in 1907, Burra Creek west of World's End in 1922, at Pualco in 1932, and Jamestown-White Yarcowie in 1939. Such has also been recorded by Jack at Mt. Grainger (1916) and Dickinson at Burra (1941).

Segnit (1939), reexamining Jack's Mt. Grainger tillites, came to the conclusion that there existed only one tillite horizon, which had been repeated by faulting. This I have since checked and fine Jack's recording to be absolutely correct. In our investigation of the area we found some 8,000 feet of fluvial sediments separating the main tillite horizon at Mt. Grainger from the conformably overlying Dust Holes Range tillite.

The record at Bibliando clearly indicates two extended periods of glaciation separated by a notable interglacial epoch. The question arises as to which of these divisions of the glacial record should be regarded as equivalent to the tillite of the Sturt Gorge and therefore Sturtian in the full sense of the term. However, the fact that the Sturt Gorge tillite passed directly upwards through laminated slates to the Brighton Limestone horizon demonstrates its equivalence to the upper glacial sequence of the Bibliando section. To distinguish the lower record of extended glaciation we may refer to it as the Bibliando stage. Such knowledge as we already have of the Proterozoic succession over a wide area of the geosynclinal basin indicates that evidence of the lower, Bibliando stage of glaciation may be limited to the deeper portions of the basin. Any depositions in the marginal areas would tend to be stripped by the subsequent glaciation.

Some evidence of glaciation at a later date than recorded in the strata of the Bibliando Dome (actually located above the Brighton Limestone horizon) is now under investigation. If this can be sustained then even the thick series of slates and limestones of the uppermost part of the succession herein recorded may itself be interglacial.

Evidence of a Major Enduring Ice-cap Glaciation.

The systematic collection of erratics by the author from outcrops in many parts of South Australia and the Barrier Range in New South Wales has yielded proof that the ice at this period was in the nature of one or more ice-caps of great extent, transporting erratics at various times into the central basin from the region of Olary and the Barrier Ranges in the east, also from the vicinity of Mt. Painter to the north and from the Gawler Ranges far to the west.

Furthermore, the floor of portion of the basin itself, notably in the marginal areas, was actively eroded by the ice, the lower tillite in some areas being loaded with the débris of the underlying formations (Mawson, 1947). The nature of the basal tillite in relation to the underlying formation at a locality near Kapunda recorded by Howchin (1927) is further evidence of the overriding nature of the ice sheet. Andrews (1922, p. 65) also has given clear evidence of ice sheet erosion of the underlying rock formation. So far, however, there has been no discovery of a polished and ice-scratched basement.

Evidence now accumulated indicates that the scale on which the ice operated in South Australia implies a far greater geographical extension in the Australian region than that so far proved. Professor Carey's (1946) recent discovery of tillite, apparently of this same age, on King Island in Bass Strait, and near Zeehan in Tasmania, supports this contention.

The Stratigraphical Position of the Bibliando Tillites.

As already mentioned (p. 163), the upward succession of beds above the Brighton Limestone horizon, item (188) of the Bibliando Dome section, is to be found in an earlier publication (Mawson, 1941*a*), where a further thickness of

12,330 feet of sediments carries the stratigraphic column to the base of the Pound Quartzite, which can no longer be considered other than Cambrian. Briefly summarised, this succession is now stated in descending sequence :

Section Measured South of the Druid Range.

	Feet
Hard, white Pound Quartzite of the Druid Range, 2,470 feet.	
Soft, red sandstone, sandy shales and red shale	1,070
Flaggy shales, in part calcareous, also some bands of impure limestone	2,410
Upper Chocolate Series	1,690
A.B.C. sandstone	240
Flaggy slates with sandstone bars above	1,120
Middle Chocolate Series	2,550
Grey shales with some narrow, minor bands of arenaceous limestone	680
Lower chocolate series of shales with some narrow bands of limestone and a little soft sandstone	1,870
Flaggy calcareous argillites, and a little grey limestone	700
Oolitic, and in part arenaceous limestone with some cryptozoonic markings	240

Section Measured Across the Bibliando Dome.

	Feet
Calcareous arenaceous shales and some sandstones	577
Lacustrine shales with recurrent bands of greywacke	8,763
Glacio-lacustrine shales and minor arenites	2,856
Upper Glacial Series	4,556
Interglacial arenites (sandstone and arkose)	2,062
Lower Glacial Series (as far down as exposed)	4,095
Total thickness below the Cambrian Pound Quartzite	35,479

As already mentioned, the Lower Glacial Series is not expected to continue much below the lowest horizon recorded in the Bibliando section. In all probability, the immediately pre-glacial sediments in the area under discussion will be found to be shales with much dolomite and magnesite (Mundallio horizon) overlying thick sandstones (Emeroo Range horizon).

At Mundallio Creek (Mawson, 1947) closer to the margin of the geosynclinal basin, the tillite rests on an eroded surface of the underlying beds, and there remains below it only 7,453 feet of the latter above the base of the system. Near Copley (Mawson, 1941), 140 miles to the north, pre-glacial erosion appears to have been much less, for there exists below the glacials some 6,228 feet of the dolomite-magnesite series overlying the 5,217 feet of basal quartzite (Aroona Waters or Emeroo Range quartzite) : total 11,445 feet. The Precambrian sediments of the great late Proterozoic-Cambrian geosynclinal trough of South Australia therefore in its thickest development amounts to not less than about 47,000 feet.

The term Adelaide Series, or better Adelaide System, was some 25 years ago proposed to signify the thick, virtually unfossiliferous sediments of this basin in the neighbourhood of Adelaide, extending upwards from the violently unconformable basal sandstones to the base of the fossiliferous Cambrian above. Howchin, however, adopted this term to include only the Brighton Limestone and underlying beds ; he preferred, even to the last, to consider as Cambrian all beds between the Brighton Limestone and the fossiliferous Cambrian. To further clarify Howchin's viewpoint it may be mentioned that in all his earlier publications he referred to the succession up to and including the Brighton Limestone as Lower-Cambrian, and to the beds above as Upper-Cambrian. At a later date he conceded that the Brighton Limestone and underlying beds might possibly be Precambrian, and he accepted the fossiliferous Cambrian as Lower-Cambrian.

The vast thickness (47,000 feet) of sediments in the region of Bibliando is representative of the northward extension of the Adelaide System. In the vicinity of Adelaide, Sprigg (1942 and 1947), reviewing Howchin's figure of 13,000 feet, states the thickness of strata, from the base to the quartzite counterpart of the Pound formation of the northern areas, to be about 23,000 feet. Even this is considerably less than its counterpart in the more central region of the basin.

It is noteworthy that in the Australian region, in late Proterozoic time, the climate passed from glacial to arid, as indicated by the chocolate shales of the upper portion of the Adelaide System. A similar development is recorded after both the late Palæozoic and the Pleistocene glaciations. But Australia is no exception in this regard, as aridity is widely recorded following upon great ice-ages in other parts of the world. This is, indeed, so much the case that it can be considered an established sequence, which suggests that the application of the factor responsible for subsequent aridity was also concerned in the passing of ice-ages. The factor most obviously involved is of course reduced precipitation: what may have in time led up to this is not so obvious, and could conceivably be accounted for as the result of one or more of several controls.

Age of the Glaciation.

The glacigene sediments recorded are interbedded in the Adelaide System, which is but little affected by regional metamorphism and, so, much resembles normal Palæozoic sediments. They are, however, unfossiliferous. Howchin earlier maintained his Sturtian tillite to be of Cambrian age as it underlay, without an apparent break, though at a considerable depth, fossiliferous Cambrian strata.

Now, however, the odds are all in favour of the Sturtian glaciation, being of Proterozoic age; probably late Proterozoic. The main considerations that lead to this conclusion are:

1. The lower horizon of fossiliferous Cambrian strata in the basin is now regarded as of Lower-Cambrian age (David, 1932).
2. The lowest fossiliferous horizon, the Pound Sandstone, appears to disconformably overlie the subjacent beds.
3. The vast thickness of post-glacial sediments underlying the fossiliferous Cambrian implies a long period of time.

It is appropriate that some explanation and qualification be made to the assertion that the sediments below the Pound Quartzite are unfossiliferous. Actually, the limestones do contain abundant structures which have long been accepted by me as resulting from organic agency; these are the cryptozoonic forms now widely recorded in Proterozoic strata from many parts of the world. The view now widely advocated that such are the result of the biochemical activities of certain types of algæ has, for long past, been accepted by the author as the most probable explanation. These structures, however, in the present state of knowledge cannot be accepted as of chronological value.

Discoveries of radiolaria reported by Howchin and David and, later, of segments of crustacea reported by David have not been confirmed by other workers (see Sprigg, 1942, 1947).

In fact, no evidence has yet been forthcoming that clearly indicates a marine origin for any part of the Adelaide System. The facts are compatible with a continental origin as advocated by Grabau (1940) for the Sinian system of China and by Blackwelder (1932) for an extensive late Proterozoic System embodying tillite horizons widely extended in Utah and Wyoming.

In recent years a number of ancient tillites discovered in various parts of the world have been reported as of Cambrian age, a decision consequent upon the finding of Cambrian fossils in superimposed beds, though there may be a considerable thickness of unfossiliferous strata between the evidences of glaciation and the fossiliferous horizons. In some cases reexamination of the areas has revealed evidence of disconformity or nonconformity in the intervening strata. There has thus been a fairly general tendency to refer this glacial epoch back to the later Proterozoic. Aspects of this controversy have been well discussed by Oskar Kulling (1936), who has contributed greatly to the evidence available. There appears thus to be a clear case for major world-wide glaciation in the late Proterozoic, and the evidence forthcoming in Australia supports this conclusion.

How far back into the Proterozoic the glacigene sediments of the Bibliando Dome extend is another matter. We have shown that the earlier tillite is some 35,000 feet below the base of the Lower-Cambrian. The accumulation of this thickness of sediment must signify the passage of a considerable period of time.

It is worthy of note that some of these late Precambrian tillites, as for example the Sturtian of Australia, the Griquatown tillite of South Africa (Du Toit, 1939) and the Sveanor tillite of Spitzbergen (Kulling, 1936), though geographically remote from each other, are constituents of sedimentary successions which exhibit certain notable correspondences ; so much so that contemporaneity of their deposition is strongly suggested.

World-wide Nature and Marked Intensity of this Greatest Ice-Age.*

Records of severe glaciation in the late Precambrian are fast accumulating. So far as can at present be judged, frequent and widespread refrigerations were a feature of at least middle to late Proterozoic time. Glaciation is evidenced even to the Equator itself.

Authentic records of such from beyond the limits of Australia are now known from India, China, Central Asia, Siberia, Finmark, Norway, Spitzbergen, North-east Greenland, Canada, Utah and neighbouring states, and many places in South and Central Africa. The accompanying sketch map (Fig. 3) roughly indicates their distribution.

Some Records of Precambrian Glaciation.

(See Fig. 3.)

1. Sturtian tillite : South Australia and N.S.W. (herein discussed).
2. King Island tillite : King Island, Bass Strait (Carey, 1946).
3. Nantau tillite : China (Lee, 1924).
4. Blaini tillite : Himalaya (Holland, 1908).
5. Varogva tillite : Yenisei Range, Central Siberia (Nicolaev, 1930).
6. Kuten-Buluk Range tillite : Southern Siberia (Tchurakov, 1933).
7. Kuruk-Tagh tillite : Central Asia (Erik Norin : see Kulling, 1936).
8. Sveanor tillite : Heckla Hoek Formation, Spitzbergen (Kulling, 1936).
9. Bossekop tillite : Finmarken (Coleman, 1926 ; Kulling, 1936).

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* When preparing this address I overlooked Professor B. F. Howell's contribution to the subject read before the International Geological Congress at Moscow in 1938. This important paper, a copy of which I have just received (Aug., 1948), is entitled : " Late Proterozoic and Early Cambrian Climates ".

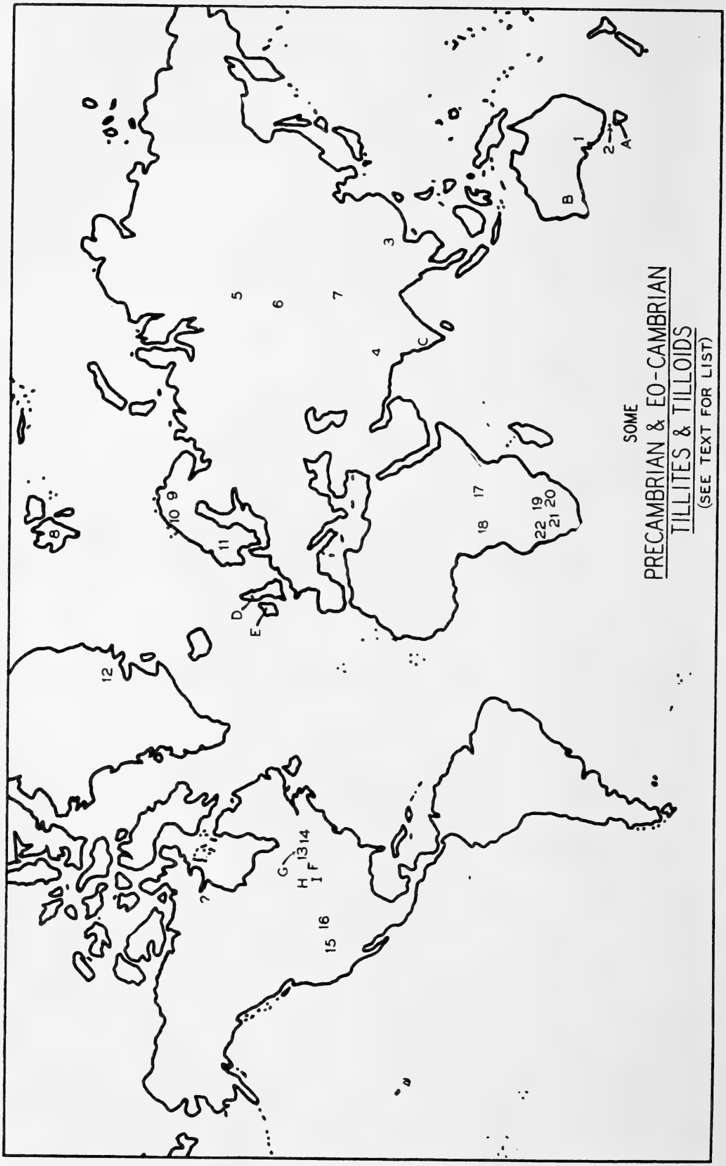

Fig. 3.—Some Localities where Precambrian Tillites or Tilloids have been Reported.

10. Varanger tillite: North Norway (Kulling, 1936).
11. Sparagmite tillite (Kulling, 1936).
12. Cape Oswald tillite: North-east Greenland (Kulling, 1936).
13. Bruce Series tillite (?): Ontario (Coleman, 1926).
14. Gowganda tillite: Ontario (Coleman, 1926).
15. Utah tillites: Various occurrences in Utah (Blackwelder, 1932).
16. Medicine Bow River metatillites: Wyoming (Blackwelder, 1926).
17. Bunyoro tillite (?): Uganda (Geol. Survey specimen submitted 1928).
18. Kundelungu tillite: Congo (Beetz, 1929).
19. Daspoort tillite: Pretoria Series, Transvaal (Du Toit, 1939).
20. Government Reefs tillite: Witwatersrand System, Transvaal (Du Toit, 1939).
21. Numees tillite: Transvaal System, Southern South-West Africa (Du Toit, 1939).
22. Chuos tillite: Damara System, South-West Africa (Du Toit, 1939).

Tilloids with Characteristics Suggestive of Glacial Origin.

A. Zeehan tilloid*: Tasmania (Professor Carey, personal com.).
B. Kanowna tilloid: Western Australia, (herein mentioned).
C. Kaldrug tilloid: (Dharwar), India (Coleman, 1926).
D. Gairloch tilloid: (Torridonian), Scotland (Coleman, 1926),
E. Dalradian tilloid: Donnegal, Ireland (Coleman, 1926).
F. Pointe aux Mines tilloid: (Keweenawan), U.S.A. (Coleman, 1926).
G. Timiskaming tilloid: Canada (Coleman, 1926).
H. Shoal Lake tilloid: (Seine Series), Canada (Coleman, 1926).
I. Doré tilloid: (Keewatin), Canada (Coleman).

As for evidence of late Precambrian glaciation within the Commonwealth of Australia, reference has already been made to the region involved in South Australia and western New South Wales. Then there is Carey's (1946) recent discovery of tillite on King Island.

A more ancient period of glaciation is evidenced at Kanowna in Western Australia. There a tilloid meta-conglomerate associated with much laminated meta-argillites exhibits so many of the characters indicative of glacial origin that, after a very brief inspection in 1926, the author accepted it as such.

Nor is this all, for in South Australia also, proof of an older Precambrian glaciation has been gradually mounting and may soon be conclusive.

Verily, the Precambrian during at least its later stages was an era of marked glaciation. When allowance is made, firstly for the obliteration as the result of long-continued erosion of a very large part of such ancient formations, secondly for the limited areas of Precambrian strata exposed for inspection, thirdly for the fact that so much of such ancient formations has been metamorphosed out of recognition of its original character, then it must be conceded, in view of the abundance and wide distribution of Precambrian tillites already located, that glaciations of Precambrian time were probably the most severe of all in earth history; in fact the world must then have experienced its greatest Ice-Age.

PROBABLE INFLUENCE ON THE RECORD OF PRECAMBRIAN LIFE.

As Grabau (1940, p. 65) states, " No one any longer questions the existence of life long before the time of the earliest Cambrian organisms that we have any record of. But the nature of the organisms, and the reason for the all but

---

* Now proved to be a Tillite.

complete absence of a record of their existence has been one of the major puzzles of our science."

It is universally conceded that the sea is the mother of life and that all early evolutional development proceeded in the sea. If as has been advocated, the volume of the hydrosphere was materially less in Precambrian times than in succeeding ages, the elevated sialic continental areas must have stood notably high above the primordial ocean-filled basins, where alone records of contemporary life could be preserved.

The severity and long duration of the period of refrigeration preceding the Cambrian must have exerted a profound influence upon evolution and the distribution of life of that time. Limitations imposed by glacial conditions may well have been an important factor in confining life to narrow geographical regions, the sedimentary records of which have never yet been discovered: perhaps lost beneath the present expanded oceans or deposited in such zones as have been deeply depressed and overwhelmed in crustal revolutions the sediments themselves perhaps palingenetically reconstructed.

Then with the advent of Cambrian time and the melting of ice-caps, shallow epiiric seas rich in life spread over the continental lowlands to deposit the first great record of marine life.

SUMMARY.

The Precambrian sedimentary record of the central region of the late Precambrian to Middle-Cambrian geosynclinal basin of South Australia, as deduced mainly from measurements made across the Bibliando Dome, is detailed and is shown to amount in all to close on 50,000 feet.

Special attention is paid to the glacigene section of the record; this is shown to have accumulated in two main divisions separated by a notable interglacial epoch.

Evidence is given of large-scale ice-cap glaciation in Australia during the late Proterozoic. Records of glaciation at this same time are quoted from other parts of the world; these also indicate extensive and severe glaciation. Attention is drawn to the effect of such climatic extremes upon evolution and the distribution of life during Precambrian times.

ACKNOWLEDGEMENTS.

We are much indebted to the Air Force Photographic Division for copies of aerial photographs of the Bibliando Dome region. For help in the field I wish to thank students who have accompanied me on various occasions, more especially R. C. Sprigg and W. B. Dallwitz. H. E. E. Brock has been responsible for drafting of the aerial photo plot and folding section.

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Explanation of Plates.

Plate X.

Aerial view looking north over portion of the Bibliando Pound in the neighbourhood of Bibliando homestead. The white cross marks the location of Wilyerpa summit.

Plate XI.

Fig. 1.—Distant view of the accordant summit level of the Wilyerpa ridge as viewed from the north-west.

Fig. 2.—View in vicinity of Wilyerpa summit of the quartzite ridges forming the rim of the Bibliando Pound.

Plate XII.

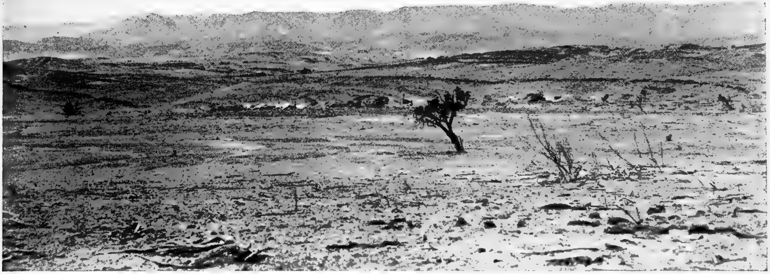
Fig. 1.—Northward dipping strata of the interior of the Pound on the north side.

Fig. 2.—Horizontally disposed strata of the central region of the Pound.

Plate XIII.

Fig. 1.—Varved glacigene sediments from the neighbourhood of Glen Warwick.

Fig. 2.—Intraformational, penecontemporaneously crumpled, glacigene sediments.



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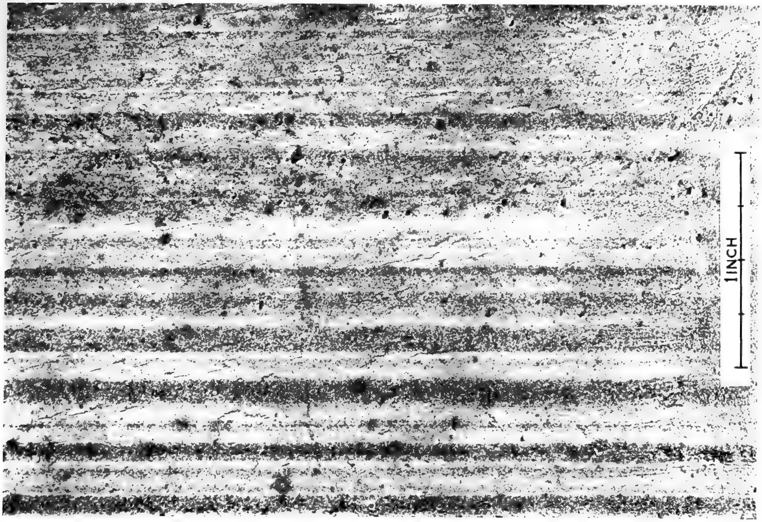

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Part III

THE INCOMPLETE NATURE OF THE SYMMETRY RELATIONS BETWEEN THERMODYNAMICAL QUANTITIES.

By R. C. L. Bosworth.

Manuscript received, June 20, 1948. Read, August 4, 1948.

Classical chemical thermodynamics is based on the properties of four variables each with the physical dimensions of energy per gramme molecule. These variables, with the symbols as accepted by the Joint Committee, London (1937), are :

(*a*) The internal energy : U.
(*b*) The free energy : A.
(*c*) The enthalpy : H.
(*d*) The Gibbs' function or free enthalpy : G.

In a simple single phase system these variables are functions of two pairs of canonically conjugate parameters, namely

The pressure, p, and the molar volume, V ;
The temperature, T, and the molar entropy, S,

of such a kind that the energy change in any system is

$\triangle U$ if the parameters S and V are maintained constant,
$\triangle A$,, ,, ,, T ,, V ,, ,, ,,
$\triangle H$,, ,, ,, S ,, p ,, ,, ,,
$\triangle G$,, ,, ,, T ,, p ,, ,, ,,

The science of thermodynamics owes much of its practical usefulness to the great number of partial differential equations holding between the four variables and the four parameters. Koenig (1935) has shown that these relationships can be classified in groups and Buckley (1944) has described a system of cylindrical tangential contact transformations which can be used in the derivation of all equations in a given group from the prototype. In these transformations U, A, H, G and S, T, p, V enter in a symmetrical manner. However, when we come to consider polycomponent systems the four parameters are insufficient for a complete description of the state of the system and other canonically conjugate pairs must be introduced. The energy of such polycomponent systems obviously depends on the number of molecules of each component present. Let us denote by n_i, n_j, etc., the mole fractions of the different components or the ratio of the number of molecules of each component to the total number of molecules present. If n_i is summed over all components, the result is clearly unity. Thus we have

$$\sum_i n_i = 1,$$

so that for a system of m components there are m−1 independent parameters n_i. For each n_i we may define a canonically conjugate variable μ_i by

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j}, \ (j \neq i) \qquad = \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_j}, \ (j \neq i) \text{ etc.}$$

μ_i is known as the molar chemical potential for the *ith* component. For an m component system there are clearly m−1 independent μ_i's.

Neither Koenig nor Buckley made any attempt to absorb the n_1's and μ_1's symmetrically into their systems, and with the number of variables limited to four it would clearly be impossible to do so. For $\triangle A$, $\triangle U$, $\triangle H$ and $\triangle G$ as already defined refer only to changes which occur under conditions of constant n_1. No variables have been introduced to express the energy changes resulting from a type of reaction in which one or more of the μ_1's are maintained constant. While it is clearly only a formal matter to introduce such new variables into the body of thermodynamical theory, it would be pointless to do so unless we were first assured that the innovation could be employed in a more elegant treatment of other branches of the subject. To this end it is instructive to consider the interrelations between the different thermodynamical variables and the physical conditions which obtain in industrial chemical operations.

THE DRIVING FORCE FOR CHEMICAL OPERATIONS.

A chemical reaction, considered as a process of transfer from one state to another in a chemical assembly, proceeds under a driving force which, in combination with a resistance coefficient, determines the rate of transfer. The driving force for any chemical reaction is the associated potential energy change. Thus if the physical conditions are maintained isopiestic and adiabatic the driving force will be the enthalpy change $\triangle H$. If the physical conditions are isometric and isothermal, the driving force is the free energy change $\triangle A$. In small scale laboratory work it is generally most convenient to maintain the temperature and pressure constant (as well, of course, as the mole fractions). Accordingly $\triangle G$ is the expression most generally used for the driving force in laboratory scale reactions. However, if the same system is to be studied in larger scale equipment, then a simple dimensional argument (Bosworth, 1947*a*, 1947*b*) shows that the mechanisms available for removal of the heat of reaction become progressively less and less effective in comparison with the rate of evolution of heat by the reaction. Accordingly a reaction which proceeds effectively under isothermal conditions in small scale equipment will proceed more nearly under adiabatic conditions in very large equipment. In the former case the chemical driving force is $\triangle G$, in the latter it is $\triangle H$. For moderately large equipment where the conditions are neither adiabatic nor isothermal the driving force is intermediate in value between $\triangle H$ and $\triangle G$. Weber (1939), for example, has used for such systems a quantity which he calls the availability and denotes by the symbol B. B is defined by $B=H-T_0S$, whereas $G=H-TS$. Here T is the temperature of the reacting mixture and T_0 that of the sink at which the heat from the reaction is discharged, the temperature of the reaction mixture itself being uncontrolled. As T_0 is made progressively less than T, the difference between B and G is progressively increased.

Let us now suppose that the reaction to be studied in a series of vessels of increasing size were to proceed so rapidly that, in the larger vessels, the volume change produced by the reaction were dissipated at a rate which was slow in comparison with the rate of the reaction. Under such a hypothetical condition the driving force for the reaction, which was $\triangle G$ in the smaller vessels, would become $\triangle A$, or the change in the free energy, in the larger vessels. If neither the heat changes nor the volume changes are allowed to dissipate, the driving force becomes $\triangle U$, the change in the internal energy. A given property change will largely be permitted to dissipate if the time taken for the different diffusive mechanisms operative in transporting the property concerned from the reaction point to the walls is small in comparison with the half-life period of a molecule of a reagent in the reaction zone. Since volume changes are dissipated with the velocity of sound and the time taken for a sound wave to traverse any ordinary sized reaction vessel is small in comparison with the rate constant of any reaction of industrial importance, neither of the two instances mentioned above have, at the moment, any technical significance. However, the rate of removal of heat alone by thermal transport mechanisms in attainable sized reactors is frequently slow in comparison with the reaction rate constant and $\triangle B$ or, in extreme cases $\triangle H$, can be taken as the effective chemical driving force.

The removal of the products of reaction from the point at which the reaction occurs can be effected by diffusion, turbulent diffusion or by convection and the rate is frequently slow, often somewhat slower than the transfer of heat. If we neglect for the moment the effect of the reaction heat and consider a system in which p, T and all the n_i's except n_j are maintained constant, we have a system in which the chemical driving force is not G but $G - n_j\mu_j$. To this quantity which clearly is a new thermodynamical variable we shall give the symbol J_j. There are $m-1$ different quantities of this nature for a system of m components, or if we include among the J_j's those which refer to energy changes in which one, two or more chemical components are prevented from diffusing to or from the point of reaction there are $(m-1)!$ such variables.

Corresponding to the partial differential equation

$$\left(\frac{\partial J_j}{\partial \mu_j}\right)_{p,T,\mu_i} = -n_j, \quad i \neq j$$

we have the well-known equation

$$\left(\frac{\partial G}{\partial n_j}\right)_{p,T,n_i} = \mu_j, \quad i \neq j.$$

For a binary system there is only one independent n, and therefore only one J. Further, for a binary system forming an ideal solution G is linearly dependent on n and thus J vanishes.

Corresponding to the thermodynamical variables J_j defined above there are others related to the other three ordinary (chemical) thermodynamical variables, viz.:

$H - n_j\mu_j$
$A - n_j\mu_j$
$U - n_j\mu_j$

making in all $4((m-1)!+1)$ variables for a system symmetrical with respect to all chemical parameters. These quantities and the parameters may be represented by a geometrical figure of a considerably higher order of symmetry than the simple two-dimensional one used by Koenig. However, it is only in the case of the two-component system that this figure may be realized in a space of three dimensions.

REPRESENTATION OF THE VARIABLES FOR A TWO-COMPONENT SYSTEM.

In a two-component system there is only one independent n and therefore only one μ. In such a system there are six canonical parameters (T, S, p, V, n, μ) and eight variables (U, A, H, G, $U - n\mu$, $A - n\mu$, $H - n\mu$, $G - n\mu$) which are related to one another in such a way that each variable is a function of three parameters and each parameter is functionally related to four variables. This relationship may thus be represented geometrically either by a cube or by a regular octahedron. The octahedron has eight faces and six corners. Each corner is surrounded by four faces and each face by three corners. Let us inscribe on one particular face a thermodynamical variable (say U) and then proceed to label the three circumscribing corners with the parameters which are not partial derivatives of the variable; V, S and n if the variable is U. There are two independent ways of labelling these corners, depending on whether V, S or n are arranged clockwise or anti-clockwise around the U face. Having assigned symbols to one face and three corners, there is now only one way of filling in all the other corners and faces. The resultant two representations of the relationships between the thermodynamical quantities are shown in Figure 1. The two forms, it will be seen, are enantiomorphous or are related to one another by a reflective operation. Further, since the octahedra are regular, there are 24 equivalent orientations for each one, or 48 equivalent orientations in all. If any relationship between the thermodynamical quantities is expressed as a relationship between the faces and corners of the octahedron, then up to 47 other equivalent relationships may be obtained by rotation of the two forms of the octahedron. Both Koenig and Buckley were able to show that thermodynamical relationships could be classified in groups, but in their scheme eight was the maximum number of members in any one group. In the present scheme with up to 48 members in a group all useful thermodynamical relationships can be covered by a smaller number of groups.

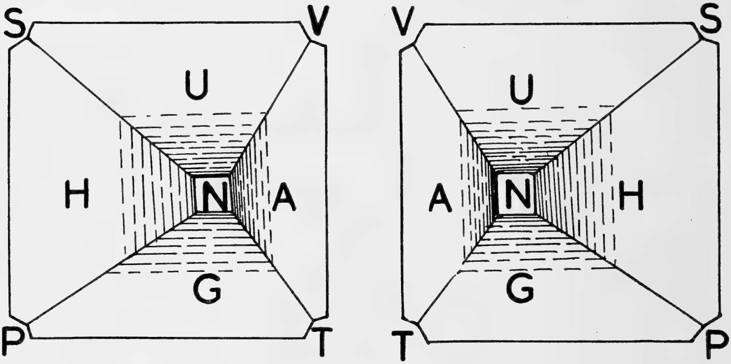

Fig. 1.—The two enantiomorphous octahedra representing the relationship between thermodynamical quantities. The back corner in each case is marked μ, and the back faces U—$n\mu$, A—$n\mu$, G—$n\mu$, H—$n\mu$ to correspond respectively to the U, A, G and H faces shown marked in the diagram.

Before, however, we discuss the grouping of thermodynamical relationships it will be necessary to discuss the question of the algebraic sign of the various quantities. Both Koenig and Buckley have discussed a " rule of signs " to be superimposed on their symmetry schemes in order that the equations derived by rotation or reflection should be correct in this respect. In terms of the new octahedral representation the rule of signs takes a particularly simple form. Three of the parameters (chosen so not to include a conjugate pair) are to be taken as alternatively positive and negative quantities according as they are represented by points of positive or negative co-ordinates in a system of cartesian axes defined by lines through opposite corners of the octahedron. The other three parameters and the variables are always to be taken as positive quantities. The most convenient triad of parameters to select as those which change sign with orientation are S, p and n, which are all equal to negative partial differential coefficients of the thermodynamical variables, i.e.

$$S=-\left(\frac{\partial A}{\partial T}\right)_{V,n}$$

$$p=-\left(\frac{\partial A}{\partial V}\right)_{S,n}$$

$$n=-\left(\frac{\partial J}{\partial \mu}\right)_{T,p.}$$

EQUIVALENT THERMODYNAMICAL REPRESENTATIONS.

The various orientations of the different octahedral faces and corners may be described by a scheme which labels the three positive corners x, y, z, the three negative corners, $\bar{x}$, $\bar{y}$, $\bar{z}$, the four front faces a, b, c, d and the four back faces $\bar{a}$, $\bar{b}$, $\bar{c}$, $\bar{d}$. Let us take as the standard orientation the one for which

$$\begin{array}{ll} x=S & \bar{x}=T \\ y=V & \bar{y}=-p \\ z=n & \bar{z}=\mu \\ & \\ a=U & \bar{a}=U-n\mu \\ b=H & \bar{b}=H-n\mu \\ c=G & \bar{c}=G-n\mu \\ d=A & \bar{d}=A-n\mu \end{array}$$

Then when the octahedron is subject to the 48 possible rotations and reflections 47 other equivalent representations will be reproduced. These equivalent representations are given in Table 1. Since U—nμ, etc., never occur directly in the standard forms for thermodynamical equations, the $\bar{a}$, $\bar{b}$, $\bar{c}$, $\bar{d}$ faces will not be given in the table. The representations referred to as $S_{(\text{subscript})}$ are obtained by rotations of the standard representation referred to as S_1. The representations marked $R_{(\text{subscript})}$ are obtained by reflections of $S_{(\text{subscript})}$.

THERMODYNAMICAL RELATIONSHIPS.

The representation of thermodynamical relationships as members of a limited number of groups is illustrated in Table 2. Here all the ordinary zero and first order relationships are covered in seven groups. Each group may be represented by a symbolic equation in x, y, z, $\bar{x}$, $\bar{y}$, $\bar{z}$, a, b, c and d, and by operating on this equation with the various operators from S_1 to R_{24} all the various members of the group may be formed. The number of members of the group obviously depends on the degree of symmetry of the symbolic equation and may be 48 or any proper fraction of 48.

Further, the members of these groups are not all independent. Thus S_{10} operating on group IV gives

$$\left(\frac{\partial U}{\partial \mu}\right)_{V,S}=\mu\left(\frac{\partial n}{\partial \mu}\right)_{V,S}$$

and an identical equation is obtained by the operation of S_{10} on group III, Further, operation of S_{22} on both groups III and IV gives a single expression. namely

$$\mu=\left(\frac{\partial G}{\partial n}\right)_{p,T}$$

and there occurs several similar cases of overlapping between the groups.

TABLE 1.

Operation.	Positive Corners.			Negative Corners.			Front Faces.			
Type.	x	y	z	$\bar{x}$	$\bar{y}$	$\bar{z}$	a	b	c	d
S_1	S	V	n	T	−p	μ	U	H	G	A
R_1	S	V	μ	T	−p	−n	U−nμ	H−nμ	G−nμ	A−nμ
S_2	p	S	n	V	T	μ	H	G	A	U
R_2	p	S	μ	V	T	−n	H−nμ	G−nμ	A−nμ	U−nμ
S_3	T	p	n	−S	V	μ	G	A	U	H
R_3	T	p	μ	−S	V	−n	G−nμ	A−nμ	U−nμ	H−nμ
S_4	V	T	n	−p	−S	μ	A	U	G	G
R_4	V	T	μ	−p	−S	−n	A−nμ	U−nμ	H−nμ	G−nμ
S_5	S	p	μ	T	V	−n	H−nμ	U−nμ	A−nμ	G−nμ
R_5	S	p	n	T	V	μ	H	U	A	G
S_6	V	S	μ	−p	T	−n	U−nμ	A−nμ	G−nμ	H−nμ
R_6	V	S	n	−p	T	μ	U	A	G	H
S_7	T	V	μ	−S	−p	−n	A−nμ	G−nμ	H−nμ	U−nμ
R_7	T	V	n	−S	−p	μ	A	G	H	U
S_8	p	T	μ	V	−S	−n	G−nμ	H−nμ	U−nμ	A−nμ
R_8	p	T	n	V	−S	μ	G	H	U	A
S_9	S	μ	V	T	−n	−p	U−nμ	U	A	A−nμ
R_9	S	μ	p	T	−n	V	H−nμ	H	G	G−nμ
S_{10}	n	S	V	μ	T	−p	U	A	A−nμ	U−nμ
R_{10}	n	S	p	μ	T	V	H	G	G−nμ	H−nμ
S_{11}	T	n	V	−S	μ	−p	A	A−nμ	U−nμ	U
R_{11}	T	n	p	−S	μ	V	G	G−nμ	H−nμ	H
S_{12}	μ	T	V	−n	−S	−p	A−nμ	U−nμ	U	A
R_{12}	μ	T	p	−n	−S	V	G−nμ	H−nμ	H	G
S_{13}	S	n	p	T	μ	V	H	H−nμ	G−nμ	G
R_{13}	S	n	V	T	μ	−p	U	U−nμ	A−nμ	A
S_{14}	μ	S	p	−n	T	V	H−nμ	G−nμ	G	H
R_{14}	μ	S	V	−n	T	−p	U−nμ	A−nμ	A	U
S_{15}	T	μ	p	−S	−n	V	G−nμ	G	H	H−nμ
R_{15}	T	μ	V	−S	−n	−p	A−nμ	A	U	U−nμ
S_{16}	n	T	p	μ	−S	V	G	H	H−nμ	G−nμ
R_{16}	n	T	V	μ	−S	−p	A	U	U−nμ	A−nμ
S_{17}	p	μ	S	V	−n	T	H−nμ	H	U	U−nμ
R_{17}	p	μ	T	V	−n	−S	G−nμ	G	A	A−nμ
S_{18}	n	p	S	μ	V	T	H	U	U−nμ	H−nμ
R_{18}	n	p	T	μ	V	−S	G	A	A−nμ	G−nμ
S_{19}	V	n	S	−p	μ	T	U	U−nμ	H−nμ	H
R_{19}	V	n	T	−p	μ	−S	A	A−nμ	G−nμ	G
S_{20}	μ	V	S	−n	−p	T	U−nμ	H−nμ	H	U
R_{20}	μ	V	T	−n	−p	−S	A−nμ	G−nμ	G	A
S_{21}	p	n	T	V	μ	−S	G	G−nμ	A−nμ	A
R_{21}	p	n	S	V	μ	T	H	H−nμ	U−nμ	U
S_{22}	μ	p	T	−n	V	−S	G−nμ	A−nμ	A	G
R_{22}	μ	p	S	−n	V	T	H−nμ	U−nμ	U	H
S_{23}	V	μ	T	−p	−n	−S	A−nμ	A	G	G−nμ
R_{23}	V	μ	S	−p	−n	T	U−nμ	U	H	H−nμ
S_{24}	n	V	T	μ	−p	−S	A	G	G−nμ	A−nμ
R_{24}	n	V	S	μ	−p	T	U	H	H−nμ	U−nμ

This limited overlapping arises from the fact that we have not adopted separate names and symbols for the quantities $G-n\mu$, $H-n\mu$, $U-n\mu$ and $A-n\mu$ which in the scheme outlined above have as much right to be considered as thermodynamical variables as G, H, U and A. A further overlapping of the groups in Table 2 would result if, say, G were replaced by $A+pV$ or $H-TS$. It would seem desirable, therefore, to allocate new symbols to the four variables above, and the following are suggested :

$J=G-n\mu$ (as above)
$I=H-n\mu$
$W=U-n\mu$
$Z=A-n\mu$.

Use of these quantities besides eliminating overlapping in Table 2 would also increase the membership of some of the smaller groups.

TABLE 2.

Grouped Thermodynamical Relationships.

Type.	Group Equation.	Typical Members.	No. in Group.
I	$da=\bar{x}dx+\bar{y}dy+\bar{z}dz$	$dU=TdS-pdV+\mu dn$	4
II	$a=c+x\bar{x}+y\bar{y}$	$\begin{cases} G=U-TS+pv \\ U=A+TS \end{cases}$	6
III	$x=-\left(\frac{\partial d}{\partial \bar{x}}\right)_{y,z}$	$S=-\left(\frac{\partial A}{\partial T}\right)_{V,n}$	24
IV	$a=d-\bar{x}\left(\frac{\partial d}{\partial \bar{x}}\right)_{y,z}$	$U=A-T\left(\frac{\partial A}{\partial T}\right)_{V,n}$ (Gibbs-Helmholtz Equation)	24
V	$\left(\frac{\partial \bar{y}}{\partial \bar{x}}\right)_{y,z}=-\left(\frac{\partial x}{\partial y}\right)_{\bar{x},z}$	$\left(\frac{\partial p}{\partial T}\right)_{V,n}=\left(\frac{\partial S}{\partial V}\right)_{T,n}$	24
VI	$\left(\frac{\partial x}{\partial \bar{x}}\right)_{\bar{y},z}=-\left(\frac{\partial x}{\partial \bar{y}}\right)_{\bar{x},z}\left(\frac{\partial \bar{y}}{\partial \bar{x}}\right)_{x,z}$	$\left(\frac{\partial S}{\partial T}\right)_{p,n}=-\left(\frac{\partial S}{\partial p}\right)_{T,n}\left(\frac{\partial p}{\partial T}\right)_{S,n}$	24
VII	$\left(\frac{\partial a}{\partial y}\right)_{\bar{x},z}=-\bar{x}\left(\frac{\partial \bar{y}}{\partial \bar{x}}\right)_{y,z}+\bar{y}$	$\left(\frac{\partial U}{\partial V}\right)_{T,n}=T\left(\frac{\partial p}{\partial T}\right)_{V,n}-p$	48

REPRESENTATION OF THE CHANGE FROM SMALL TO LARGE SCALE CONDITIONS.

As has been indicated earlier in this paper, the limited rates for the diffusion of matter and heat which obtain in all reaction vessels means that a reaction which takes place under effective conditions of constant T and n when studied on the small scale will take place under conditions of constant S and μ when studied on a very large scale. This means that any thermodynamical relationship represented by the operator R_{11} of Table 1 for small scale operation will become replaced by the operator R_9 for very large scale operation. The change of R_{11} to R_9 is a change from the representation

T, n, p, $-S$, μ, V, G, J, I, H, to
S, μ, p, T, $-n$, V, I, H, G, J.

with a change in the effective driving force from $\triangle G$ to $\triangle I$ or to $\triangle G+T\triangle S-\mu\triangle n$.

SUMMARY.

The schemes for the representation of the symmetry relations between the thermodynamical variables and parameters proposed by Koenig and by Buckley do not include the chemical variables n_i and μ_i in a symmetrical manner. A representation with a considerably higher degree of symmetry may be obtained by the introduction of four new thermodynamical variables: $J=G-n\mu$, $I=H-n\mu$, $Z=A-n\mu$ and $W=U-n\mu$. The eight variables are then represented by the eight faces of a regular octahedron and the six parameters p, T, V, S, n and μ by the six corners. These are arranged in such a way that the variable represented on any one face is a function of the three parameters on the circumscribing three corners; and each corner is surrounded by the four faces whose variables are functionally related to the parameter represented by the corner. There are two enantiomorphous forms of the octahedron which will satisfy these conditions and rotation of either will give in all 48 equivalent representations of the thermodynamical properties and the various relationships between these properties may be reduced to a small number of groups each containing either 48 or a proper fraction of 48 members.

Consideration is given to the change in the thermodynamical conditions which obtains when the size of the equipment in which a given reaction is studied is increased without limit. Conditions of constant T, n and p for small scale equipment become conditions of constant S, μ and p in very large scale equipment on account of the relative slowness of the diffusion of matter and heat in the reacting mixture. This change is equivalent to a rotary operation on the octahedron representing the thermodynamical properties.

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SOME RECENT WORK ON THE SEPARATION AND USE OF STABLE ISOTOPES.*

By I. Lauder.

Mr. President, Ladies and Gentlemen,

I wish to express my appreciation of the invitation to deliver this year's Liversidge Research Lecture as this is, indeed, a high honour. The University of Queensland is greatly handicapped by its isolation, and it is not often that a member of its staff is asked to deliver a special lecture at some other university. For this reason, too, I very much appreciate the invitation.

I have chosen for the title of this address " Some Recent Work on the Separation and Use of Stable Isotopes ". There have been many outstanding achievements in science in the past ten to fifteen years, and I think that the development of methods for separating isotopes must come within this category, not only because of its immediate interest to chemistry, but also because a vast amount of important information has been gained by the use of the separated isotopes.

The existence of isotopes of radio-active elements was first established in 1911, and two years later J. J. Thomson demonstrated for the first time the existence of isotopes of a stable element—neon—of mass numbers 20 and 22. With the subsequent development of the mass-spectrograph by Aston, the isotopic compositions of most elements are now known.

Although the basic principles of most of the methods now used for the separation of isotopes have been known for many years, it was not until 1932 and later that any large-scale separations were achieved. It is interesting to note that work on the detection and separation of isotopes was suspended during World War I, whereas during World War II such work reached an immense climax with the development of the atomic bomb.

Part I. Methods of Separation.

Except in the case of hydrogen, only small differences in chemical and physical properties of isotopes exist, and these differences decrease relatively with increasing atomic weight, thus increasing the difficulty of separation. The hydrogen isotopes were the first to be separated in an almost pure state. This was achieved in 1933 by Lewis and MacDonald(1) by the continued electrolysis of water. The process is so well known that it need not be considered further, but it may be added that in the case of isotopes of other elements only very small separations have been obtained by electrolysis.

The separation of small amounts of ions of different masses has been achieved by the use of the mass-spectrograph and, during the war years, a large-scale development of this method took place for the separation of the uranium isotopes. I am not familiar with this development and may be permitted to exclude it from further consideration.

Omitting, then, any discussion on the electrolytic and the electromagnetic methods, the following methods have been used to achieve considerable degrees

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of separation: (1) diffusion, (2) distillation, (3) chemical exchange, (4) thermal diffusion. The important applications of each of these methods will be considered and, in addition, the centrifugal method of separation may be considered. This latter method has not resulted in any important degree of separation as yet, but it may become of importance in the future, especially for the separation of isotopes of high molecular weight.

(1) *Diffusion Methods.*

The rate of gaseous diffusion varies inversely as the square root of the molecular weight, and so isotopic molecules should diffuse at slightly different rates. This method was first applied by Aston in an attempt to separate the isotopes of neon, but only a very limited success was achieved. The atomic weight of neon of normal isotopic ratio is 20·2, while Aston obtained ultimately two fractions with atomic weights 20·15 and 20·28 respectively.

In all methods of separation a quantity known as the separation factor is of interest. This is given by the ratio of the isotopes after applying the separation process to the ratio before applying the separation process. That is, the separation factor with respect to the heavy molecules,

$$S=\frac{N_h/N_l \text{ (after applying separation process).}}{N_h/N_l \text{ (before applying separation process)}}$$

where N_h, N_l stand for the numbers of heavy and light molecules respectively. To achieve a maximum separation by the diffusion method, it is necessary to ensure that there is perfect mixing of the gas on each side of the porous barrier through which diffusion occurs and also that the mean pore diameter of the barrier is small in comparison with the mean free path of the diffusing gas. This is a rather stringent condition, as for most gases at one atmosphere pressure and room temperature the mean free path is of the order 10^{-5} cm. The mean free path varies inversely with pressure, and so by working at lower pressures a barrier with a larger pore diameter may be used.

For a separation by gaseous diffusion under ideal conditions the separation factor (with respect to the heavy molecules) is given approximately by the expression

$$S=\sqrt[\frac{M_2+M_1}{M_2-M_1}]{\frac{\text{Initial Volume}}{\text{Final Volume}}} \qquad (2)$$

where M_2 and M_1 stand for the molecular weights of the heavy and light molecules respectively. If half of the initial volume of gas is allowed to diffuse through the barrier, then, for the neon isotopes of molecular weights 22 and 20, $S=1{\cdot}034$. Thus only a small degree of separation is achieved in each diffusion unit, but by connecting a sufficient number of units in series any desired concentration of isotope may be achieved. The over-all separation factor for n units in series equals S^n.

The first successful apparatus for the continuous separation of isotopes by gaseous diffusion at low pressure was devised by Hertz(2) in 1932, using porous porcelain tubes as the diffusion barrier. With 48 units operating in series, Hertz(3) produced practically pure ^{22}Ne from normal neon. In the same apparatus, starting from hydrogen containing 10% deuterium, spectroscopically pure deuterium(4) was isolated. Carbon(5) containing 16% ^{13}C and nitrogen(6) containing 3% ^{15}N have been isolated by this type of diffusion method.

Later, in 1934, Hertz(7) produced a still more efficient unit in which a stream of mercury vapour served as the diffusion barrier, and at the same time it served to pump the gas undergoing diffusion from one unit to another. This modification has been used to produce oxygen(7) containing 0·5% ^{18}O, argon(8) containing 50% ^{36}A, carbon(9) containing 30% ^{13}C, and nitrogen(10) containing 9% ^{15}N.

Any account of the diffusion method of separation of isotopes could not be regarded as complete without some mention of its recent application to the separation of the uranium isotopes ^{235}U and ^{238}U using uranium hexafluoride, UF_6, as the carrier gas. A limited amount of information on the process is given in the Smythe Report.(11) Assuming that the separation factor for a single unit is 1·0013 and that 4,000 units are operated in series, the over-all separation factor comes out to 173·8. If the first unit is fed with UF_6 of normal isotopic ratio (0·7% $^{235}UF_6$), UF_6 containing approximately 55·5% $^{235}UF_6$ would be produced in the last unit when equilibrium is established. The concentrating cascade of 4,000 units would be run in combination with a stripping cascade for treating the impoverished gas from stage 1. By a partial removal of $^{238}UF_6$ in the stripping cascade, the $^{235}UF_6$ content of the impoverished gas is built up to its normal value. The gas from the first unit of the stripping cascade is then recirculated to the first unit of the concentrating cascade. If it is economical to discard the UF_6 when the $^{235}UF_6$ content has been reduced to half the normal value, the stripping cascade would consist of about 538 units operating in series.

For each cubic centimetre of 55·5% $^{235}UF_6$ withdrawn from the last unit of the concentrating cascade 157 c.c. of 0·35% $^{235}UF_6$ would be drawn off from the last unit of the stripping cascade. These withdrawals would be balanced by the input of 158 c.c. of normal UF_6 to stage 1. For each cubic centimetre of output from the last unit of the concentrating cascade about 120 litres of UF_6 would pass through the first unit, and so the total circulation in all stages would be very high indeed.

(2) *Distillation.*

The separation of liquids of different boiling points by fractional distillation is a well-understood process. Experiment shows that a fractionation column of the packed type gives concentrations in accordance with the formula

$$\frac{C_t}{1-C_t}\Big/\frac{C_b}{1-C_b}=\alpha^K \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where C_t and C_b are the mole fractions of one constituent at the top and bottom respectively. α is the ratio of the vapour pressures and K is the number of theoretical plates. Values of α for $H_2{}^{16}O$ and $H_2{}^{18}O$ forms of water at various temperatures are given in the following table.(12)

TABLE 1.

Temperature ° C.	α
11·25	1·013
35·6	1·008
46·35	1·007
100·0	1·003

When α is nearly unity, as it is in the case of the separation of most isotopes, K must be large if a large change in the concentration of isotopes is desired. To secure a large K, the length of the column should be made large, and also the efficiency of the column should be made as high as possible by the use of a suitable packing material. The value of α increases with decreasing temperature and so the degree of separation is increased by working at as low a temperature as is conveniently possible.

The method has found its chief application to the separation of the isotopic forms of water. In one column six inches in diameter and 35 feet high set up by Pegram, Huffmann, and Urey,(13) after 300 hours operation water containing 0·85% ^{18}O was produced. If equilibrium had been set up, approximately 20 c.c. of water containing about 2·5% ^{18}O could have been withdrawn daily. In the same still Roberts and Urey(14) fractionated normal methyl alcohol to produce alcohol enriched in the heavy oxygen isotope ^{18}O. No separation of the heavy carbon forms of the alcohol was obtained.

The vapour pressures of the isotopic hydrogen forms of water differ more than the vapour pressures of the isotopic oxygen forms of water.(12) Accordingly, it is found that deuterium concentrates at a faster rate than the heavy oxygen during the fractionation process. The Smythe Report mentions that one of the methods used for the separation of deuterium required for the work on atomic energy was by the fractionation of water, but no details of the still used are given.

Recently, Dostrovsky and Hughes(15) have published a short note giving details of a very efficient packed column 0·8 inch internal diameter and 12 feet high which produced after 24 hours' operation 500 c.c. of water containing 0·2% D and 0·55% ^{18}O. It is apparent from these figures that the column is highly efficient and is capable of supplying relatively large quantities of the heavy isotopes of hydrogen and oxygen at concentrations usually sufficient for exchange experiments.

(3) *Chemical Exchange.*

If the chemical properties of isotopes were identical, the equilibrium constants for isotopic exchange reactions would be unity. That this is not so was first indicated by the calculation of equilibrium constants of certain exchange reactions by Urey and Rittenberg.(16) For reactions involving isotopes of elements of low atomic weight, the constants usually differ from unity by a few per cent., but this difference decreases with increasing atomic weight and also with increasing temperature. The chemical method of separating isotopes is thus restricted to isotopes of low atomic weight and it is best carried out at as low a temperature as is conveniently possible.

For the separation of ^{15}N the following exchange reaction was used:

$$^{15}NH_3\,(g) + {}^{14}NH_4^+\,(aq) \rightleftharpoons {}^{14}NH_3\,(g) + {}^{15}NH_4^+\,(aq)$$

$$K_{25^\circ C.} = 1{\cdot}023.$$

The ^{15}N collects preferentially in the liquid phase.

The technique of the method is to establish a counter-current flow of ammonium nitrate solution and ammonia gas in a packed fractionating column. If several columns are operated in series, the sizes are reduced proportionally so as to keep the transport of the heavy isotope in each column practically the same. If the first column increases the concentration of ^{15}N by a factor of 10, for example, 9/10 of the liquid draining out of the bottom of the column is mixed with sodium hydroxide solution. The ammonia liberated is fed back into the bottom of the first column together with the ammonia issuing from the top of the second column. The remaining 1/10 of the flow from column 1 is fed into the top of the second column, and so on.

Using a three-stage apparatus of total length 43·5 metres, Urey(17) and co-workers isolated nitrogen containing 70·6% ^{15}N.

Heavy carbon, ^{13}C, has been concentrated by making use of the exchange reaction(18)

$$H^{12}CN\,(g) + {}^{13}CN'\,aq \rightleftharpoons H^{13}CN\,(g) + {}^{12}CN'\,aq.$$

$$K_{25^\circ C.} = 1{\cdot}015.$$

The ^{13}C tends to collect in the gas phase. In a two stage apparatus up to 22% ^{13}C has been produced at the rate of 0·1 gm. ^{13}C per day.

For the concentration of ^{34}S use was made of the exchange reaction[(19)]

$$^{34}SO_2 + H^{32}SO'_3 \rightleftharpoons {}^{32}SO_2 + H^{34}SO'_3.$$
$$K_{25}{}^\circ C. = 1 \cdot 012.$$

In a three-stage apparatus sulphur containing 25% ^{34}S was produced at the rate of 3·2 gm. per day.

As mentioned in the Smythe Report, the exchange reaction between water vapour and gaseous hydrogen in the presence of a suitable catalyst was used during the atomic bomb work for concentrating heavy hydrogen. The equilibrium favours the accumulation of deuterium in the water.[(20)]

$$H_2O + HD \rightleftharpoons HDO + H_2$$
$$K_{25}{}^\circ C. = 2 \cdot 67 \; ; \quad K_{100}{}^\circ C. = 2 \cdot 00.$$

(4) *Thermal Diffusion.*

In 1938 Clusius and Dickel[(21)] introduced a method of separation of isotopes by thermal diffusion which has proved very effective in many cases. Essentially, the apparatus consists of a vertical water-jacketed tube down the centre of which is stretched a wire which may be heated electrically to the desired temperature. The partial separation of light and heavy molecules which this type of apparatus may produce in a gaseous mixture is due to two effects: (1) due to thermal diffusion, the heavy molecules tend to concentrate near the cool wall of the tube and the light molecules near the hot wire; (2) due to the difference in density between the cold gas and the hot gas, a thermal siphon is set up in the tube which transports the light molecules to the top of the tube and the heavy molecules to the bottom of the tube. The separation produced by these two effects increases until it is just counterbalanced by the remixing effect of ordinary diffusion.

The various factors which influence the efficiency of such separation columns have been investigated by many workers.[(22)] For a gas containing molecules of weights M_1 and M_2 and mol. fractions C_1 and C_2 respectively, subjected to a thermal gradient (in the absence of convection currents), the relative difference in mol. fraction of either constituent is given by

$$\triangle C = k_T \log_e T_2/T_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where T_2 and T_1 $(T_2 > T_1)$ represent the temperatures at the two ends of the gradient and k_T is the coefficient of thermal diffusion. For isotopic molecules behaving as elastic spheres,

$$k_T = \frac{105}{118} \times \frac{M_2 - M_1}{M_2 + M_1} \times C_1 C_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Due to deviations from the perfect gas state, the k_T values for real gases are found to be less than the calculated values. Approximate values of k_T for actual gases may be obtained from viscosity data.[(23)] If S is the repulsive force index of the molecules and η the coefficient of viscosity, then

$$k_T \text{ (actual gas)} = k_T \text{ (perfect gas)} \times \frac{S-5}{S-1} \quad \ldots\ldots\ldots\ldots \quad (7)$$

and

$$\log \eta = \frac{S+3}{2(S-1)} \log T + \text{constant} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

If $S > 5$, the heavy molecules tend to concentrate near the cold end of the gradient; if $S < 5$, the separation occurs in the opposite direction; if $S = 5$, no separation by thermal diffusion is possible. Some values for $(S-5)/(S-1)$ for various gases are given in Table 2.

This data suggests that carbon monoxide would prove more suitable than oxygen for the separation of the oxygen isotopes, but other factors such as ease of preparation in a pure state and thermal stability must be considered.

The concentration of heavy isotope at the bottom of a separation tube when equilibrium is set up is found to be proportional to (1) r^{-4}, where r is the radius of the tube, (2) the length of the tube provided the mol. fraction is within the range 0·25–0·75, (3) p^{-2} provided the pressure is not too low.

The rate at which equilibrium is established in a column is proportional to r^4 and to p^2. In practice, it is found that the time required to establish a given concentration difference may be decreased by starting the apparatus at a pressure greater than the optimum working pressure and subsequently as the separation proceeds by reducing the pressure to the optimum working pressure.(24)

The separation of the chlorine isotopes ^{35}Cl and ^{37}Cl in an almost pure state using HCl as the carrier was achieved by Clusius and Dickel in 1939, using a five-stage apparatus of total length 36 metres and a wire temperature 690° C. The diameter of one tube was 12·8 mm., while all the other tubes had the same diameter, namely 8·4 mm. After 17 days' continuous operation, 8 c.c. $H^{37}Cl$ and 25 c.c. $H^{35}Cl$ could be withdrawn per day. The ^{35}Cl was 99·6% pure and the ^{37}Cl 99·4% pure.

TABLE 2.

Gas.	S.	$\frac{S-5}{S-1}$
He	13·1	0·67
Cl_2	5·1	0·02
O_2	9·7	0·54
CO	11·8	0·63
SO_2	4·6	−0·10

The separation of the chlorine isotopes represents a particularly favourable case, as normal chlorine contains 76% ^{35}Cl and 24% ^{37}Cl. The separation of isotopes of low abundance presents a more difficult problem.

In addition to the separation of the chlorine isotopes, Clusius and Dickel have separated the following isotopes in an almost pure form: ^{20}Ne and ^{22}Ne(26); ^{84}Kr and ^{86}Kr(27); $^{18}O_2$.(28) In an attempt to separate heavy nitrogen, Clusius and Dickel(28) obtained almost pure $^{14}N\,.\,^{15}N$. The equilibrium $2\,^{14}N\,.\,^{15}N \rightleftharpoons {}^{14}N_2 + {}^{15}N_2$ was not established at the temperature of the wire in the separation tube. Partial separations(29) of isotopes of carbon, nitrogen and hydrogen have also been reported.

Recently, a considerable degree of separation of the heavy isotopes of carbon and of oxygen was achieved by Taylor and Bernstein(30) by a combination of a chemical exchange process and thermal diffusion in a mixture of CO_2 and CO.

Bramley and Brewer(31) introduced a slight modification of the Clusius and Dickel apparatus by using two concentric tubes, the inner one being heated and the outer one cooled. A greater volume of gas may be treated by this apparatus but it is not so easy to maintain the high temperature gradient as is generally used in the Clusius and Dickel apparatus.

(5) *Centrifugation.*

The possibility of separating isotopes by a centrifugal method has been considered from time to time, but little advance had been made until the introduction of the Beams(32) air-driven centrifuge.

The separation factor as already defined is given by the equation

$$S=\exp \frac{(M_2-M_1)v^2}{2RT} \qquad (4)$$

where v is the peripheral velocity and M_2 and M_1 are the molecular weights of the constituents of the gas. It will be noticed that S depends on the difference of the masses of the two isotopes and for a given value of M_2-M_1 the method should be just as effective for the separation of isotopes of high molecular weight as for isotopes of low molecular weight.

For the uranium isotopes ^{235}U and ^{238}U, $M_2-M_1=3$, and with $v=5\times10^4$ cm./sec. and $T=300°$ K., $S=1{\cdot}16$ as compared with the value $S=1{\cdot}0013$ for a single stage of the diffusion method already considered. Under the above conditions the separation produced by one centrifugation would equal the separation produced by 115 diffusion units operating in series. A pilot centrifugal plant for the separation of the uranium isotopes was put into operation during the war years, but no large-scale plant was set up.

To achieve large separations a cascade system of centrifuges would be required and it is possible that future development will be along these lines.

The results achieved by the application of the various methods of separation are listed in Table 3.

TABLE 3.

Separations Achieved.

Method.	Isotope.	Normal Abundance of Isotope in Per Cent.	Degree of Separation in Per Cent.	Date Achieved.
Electrolysis	^{2}H	0·02	$\sim$100	1933
Diffusion	^{2}H	0·02	$\sim$100*	1933
,,	^{22}Ne	9·73	$\sim$100	1934
,,	^{18}O	0·2	0·5	1934
,,	^{36}A	0·307	50	1937
,,	^{13}C	1·1	30	1938
,,	^{15}N	0·38	9	1938
Distillation	^{18}O	0·2	0·85	1937
Chemical exchange	^{15}N	0·38	70·6	1939
,, ,,	^{13}C	1·1	22	1940
,, ,,	^{34}S	4·2	25	1940
Thermal diffusion	^{37}Cl	24	99·4	1939
,, ,,	^{35}Cl	76	99·6	1939
,, ,,	^{20}Ne	90	$\sim$100	1940
,, ,,	^{22}Ne	9·73	$\sim$100	1940
,, ,,	^{84}Kr	57·10	$\sim$100	1943
,, ,,	^{86}Kr	17·47	$\sim$100	1943
,, ,,	^{18}O	0·2	$\sim$100	1943
,, ,,	^{15}N	0·38	$\sim$ 50	1943

* This separation was achieved by using hydrogen containing 10% deuterium as the starting material.

PART II. USES OF ISOTOPES.

In recent years, both stable and radio-active isotopes of many elements have found extensive application to the study of problems in physics, chemistry and biology. If a suitable radio-active isotope of the element in question is available it is perhaps easier to use as a tracer than a stable isotope. However, in the cases of hydrogen, oxygen, nitrogen and carbon the stable isotopes have so far proved of greater value than the corresponding radio-active isotopes.

The fundamental principle underlying the use of any isotopic tracer element is that the tracer behaves in any reaction in exactly the same way as the normal element. This is true within the usual limits of experimental error provided the concentration of the isotopic tracer is not too great.

The general chemistry of the exchange reactions of heavy hydrogen is well known, and in the remaining discussion we shall consider chiefly applications of the isotopes of oxygen, nitrogen and carbon.

It is not my intention to deal with the biological applications of the separated stable isotopes other than by giving one brief example of the use of heavy hydrogen to study fat-metabolism in rats and mice. In principle, the technique used is as follows : The mice are fed with a fat or fatty-acid labelled with a few per cent. of deuterium and, after a suitable period, the animals are killed. The fatty acids are then isolated and burnt in oxygen. The water formed is collected and, after purification, its isotopic composition is determined usually by a density method.

The deuterium-labelled fatty acid is readily prepared. When a fatty acid is heated with D_2SO_4 an exchange of H for D occurs only at the α-carbon atom. On the other hand, when a fatty acid is heated with D_2O at 130–135° C. in the presence of alkali and an active platinum catalyst exchange occurs for all hydrogen atoms on the carbon chain.(33)

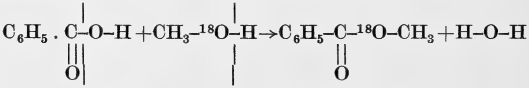
In one experiment Stetten and Schoenheimer(34) fed the ethyl ester of deuterium-labelled palmitic acid to rats and, subsequently, isolated palmitic, stearic, myristic, lauric, palmitoleic and oleic acids, all containing more deuterium than normal, showing that these acids had been formed from the dietary ethyl palmitate. Work of this type has recently been reviewed in *Science Progress*.(35)

Many applications of ^{15}N to the study of the metabolisms of proteins and amino-acids have been made and these have been reviewed by Rittenberg and Shemin.(36) Numerous papers dealing with the use of ^{13}C as a tracer in the study of fatty acid metabolism, etc., have been published in the *Journal of Biological Chemistry* from 1945 onwards.

Applications of Heavy Oxygen.

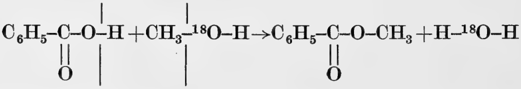
The original investigation by Polanyi and Szabo(37) of the mechanism of alkaline hydrolysis of esters using the heavy oxygen isotope as a tracer element has been extended to investigations of the mechanisms of acid-catalysed hydrolysis of esters(38) and to acid-catalysed esterification reactions.(39) Urey and Roberts investigated the mechanism of the acid-catalysed esterification reaction between benzoic acid and methyl alcohol labelled with heavy oxygen. The reaction may occur via the mechanisms illustrated by the following equations :

(*a*)



$$C_6H_5 \cdot \underset{\underset{O}{\|}}{C}{-}O{-}H + CH_3{-}{}^{18}O{-}H \rightarrow C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}{}^{18}O{-}CH_3 + H{-}O{-}H$$

(*b*)

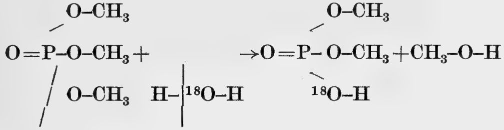


$$C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}O{-}H + CH_3{-}{}^{18}O{-}H \rightarrow C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_3 + H{-}{}^{18}O{-}H$$

If the reaction occurs by a fission of the bonds, as is illustrated by the dotted lines in equation (*a*), water of normal isotopic composition would be produced. Mechanism (*b*), on the other hand, would yield water containing the heavy oxygen originally present in the alcohol. Experiment shows that water with a normal isotopic ratio is produced during esterification, and thus mechanism (*a*) is correct.

An investigation of the mechanism of hydrolysis of trimethyl phosphate,(40) the only inorganic ester so far considered, shows that under alkaline conditions behaviour is the same as for organic esters—the alkyl-oxygen bond remains intact.

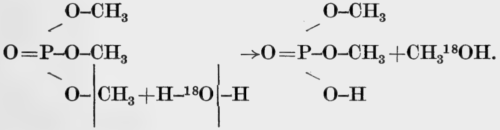
(c)



$$O{=}\overset{O-CH_3}{\underset{O-CH_3}{P}}{-}O{-}CH_3 + H{-}{}^{18}O{-}H \rightarrow O{=}\overset{O-CH_3}{\underset{{}^{18}O-H}{P}}{-}O{-}CH_3 + CH_3{-}O{-}H$$

Under acid conditions, however, the result is not so clear cut. If the bonds break as is shown by the dotted lines in equation (*c*), the alcohol formed would contain normal oxygen. The other possibility at which a break may occur is shown by the dotted lines in equation (*d*); and this would lead to the formation of alcohol containing the heavy oxygen originally present in the water.

(d)

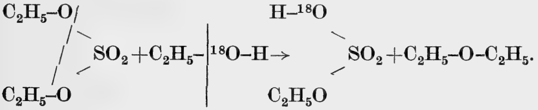


$$O{=}\overset{O-CH_3}{\underset{O-}{P}}{-}O{-}CH_3 \quad CH_3 + H{-}{}^{18}O{-}H \rightarrow O{=}\overset{O-CH_3}{\underset{O-H}{P}}{-}O{-}CH_3 + CH_3{}^{18}OH.$$

The experimental results show that both mechanisms are involved during acid hydrolysis or alternatively that the investigation is upset by the occurrence of certain side reactions.

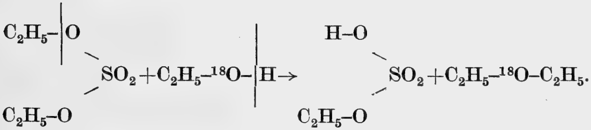
Recently, the mechanism of formation of diethyl ether(41) by reaction between diethyl sulphate and ethyl alcohol has been studied by use of heavy oxygen. In this reaction an alkyl-oxygen bond must break in one of the reagents. The two possible mechanisms are shown by equations (*e*) and (*f*).

(e)



$$\begin{matrix}C_2H_5{-}O\\C_2H_5{-}O\end{matrix}SO_2 + C_2H_5{-}{}^{18}O{-}H \rightarrow \begin{matrix}H{-}{}^{18}O\\C_2H_5O\end{matrix}SO_2 + C_2H_5{-}O{-}C_2H_5.$$

(f)



$$\begin{matrix}C_2H_5{-}O\\C_2H_5{-}O\end{matrix}SO_2 + C_2H_5{-}{}^{18}O{-}H \rightarrow \begin{matrix}H{-}O\\C_2H_5{-}O\end{matrix}SO_2 + C_2H_5{-}{}^{18}O{-}C_2H_5.$$

Experiment showed that the ether formed contained less heavy oxygen than the original alcohol. This dilution was attributed indirectly to the occurrence of two side reactions, namely hydrolysis and alcoholysis. The mechanisms of these reactions had not been investigated, and so their influence was eliminated by variation of the length of the reaction time. On extrapolation of the curve obtained by plotting ^{18}O-content of the ether against time, the ^{18}O content of the ether formed from the alcohol originally present in the mixture was obtained. This showed definitely that the ether was formed via mechanism (*f*).

The mechanisms of the benzil-benzilic acid rearrangement(42) and the Beckmann rearrangement,(43) as well as the alkali fusion(44) of certain organic compounds, have been studied by the use of heavy oxygen.

On the inorganic side, most of the applications of heavy oxygen have been for the determination of the rate of exchange of oxygen between water and the various oxy-acid ions.(45) In general, exchange occurs in acid solution, often in neutral solution and less frequently in alkaline solution. The mechanism of exchange in such reactions may involve addition and subsequent removal of a water molecule or hydroxyl ion to the anion, while in the case of the acid-catalysed exchange the most satisfactory mechanism appears to be reversible anhydride formation. For example, in the acid-catalysed exchange of oxygen between water and sulphate ions the following equilibria are believed to be involved:

$$2H^+ + SO_4'' \rightleftharpoons H_2SO_4 \rightleftharpoons H_2O + SO_3,$$

followed by $H_2{}^{18}O + SO_3 \rightleftharpoons H_2SO_3{}^{18}O$,

and so on until complete exchange is established.

Some mention may be made of the oxygen tracer work at present under investigation at the University of Queensland.

Jander's theory(46) of reactions in liquid sulphur dioxide is based on the idea that liquid SO_2 ionises to a small extent giving rise to sulphite ions and thionyl ions according to the equation

$$2SO_2 \rightleftharpoons SO_3'' + SO^{++}.$$

Recently Ingold and co-workers(47) have questioned the validity of certain of Jander's conclusions. It occurred to us that some useful information might be obtained by determining whether or not exchange of oxygen occurs between liquid sulphur dioxide and a dissolved alkali metal sulphite labelled with heavy oxygen. The above equilibrium would necessarily require an exchange to occur.

$$2Na_2S^{18}O_3 + 3SO_2 \rightleftharpoons 2Na_2SO_3 + 3S^{18}O_2.$$

Jander gives the solubilities of various alkali metal sulphites as varying from 16 to 32 mg. per 100 gm. of SO_2, but we cannot verify these figures. We have investigated the solubilities of the sulphites of sodium, potassium and ammonium as well as several other sulphur oxy-acid salts of these elements, but find virtually no solubility at all for any of these salts. We have used sulphur dioxide which has been dried very thoroughly and also sulphur dioxide containing small traces of water, but without any affect on the solubility.

It would be possible to carry out the exchange investigation by shaking liquid sulphur dioxide with the solid sulphite labelled with heavy oxygen, but it is preferable to use a sulphite which shows some degree of solubility.

While the original exchange investigation is held up pending the results of our solubility investigations, the possibility of exchange of oxygen between liquid sulphur dioxide and thionyl chloride is being investigated. According to Jander, thionyl chloride ionises in liquid SO_2

$$SOCl_2 \rightleftharpoons SO^{++} + 2Cl',$$

and, if SO_2 ionises, an exchange of oxygen would be expected.

$$S^{18}O_2 + 2SOCl_2 \rightleftharpoons SO_2 + 2S^{18}OCl_2.$$

Another problem being investigated is the interchange of oxygen between metal oxides and oxygen gas. There have not been many applications of isotopes to the study of chemical reactions in solids and it is expected that this type of work will have important bearings on the theory of such reactions. In addition to obtaining exchange results at various temperatures and pressures it will also be necessary to determine such factors as dissociation pressures of the oxide at various temperatures, surface area of oxide prepared under varying conditions and also dissociation of oxygen molecules on the surface of the oxide. Little is known about these various factors, and thus in this field alone there is sufficient research to keep several investigators occupied for quite some time.

Applications of Heavy Nitrogen and Heavy Carbon.

In the presence of a synthetic ammonia catalyst exchange between deuterium and ammonia occurs freely even at room temperature, leading to the formation of the substituted ammonias NH_2D, NHD_2 and ND_3. Taylor and Jungers(48) from these results conclude that, at the temperatures used in the synthetic ammonia process, the rate controlling step is probably the dissociation of nitrogen molecules to atoms on the surface of the catalyst. This view was confirmed by showing that the equilibrium

$$^{14}N_2+{}^{15}N_2 \rightleftharpoons 2\,{}^{14}N\,.\,{}^{15}N$$

is only slowly established on synthetic ammonia catalysts.(49) The reaction rate first becomes measurable at 450° C.

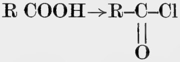
An interchange of nitrogen between nitric oxide and nitrogen dioxide in the gaseous phase at 2·5 cm. Hg pressure and —35° C. occurs at a very rapid rate.(50) This is presumably accounted for by the intermediate formation of nitrogen trioxide.

$$^{14}NO+{}^{15}NO_2 \rightleftharpoons O={}^{14}N\text{–}O\text{–}{}^{15}N=O \rightleftharpoons {}^{15}NO+{}^{14}NO_2$$

The chances of breaking either the ^{14}N–O bond or the ^{15}N–O bond would be about equal and the fission of the latter bond would lead to exchange.

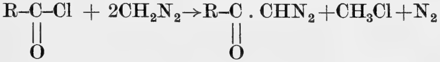
The heavy carbon isotope, ^{13}C, has been used to study the Arndt-Eistert reaction.(51) This reaction is used for the conversion of a carboxylic acid to its next higher homologue and it involves three stages:

(i) Formation of the acid chloride:



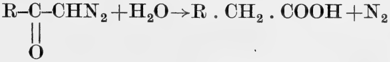
$$R\,COOH \rightarrow R\text{–}\underset{\underset{O}{\|}}{C}\text{–}Cl$$

(ii) Reaction of the acid chloride with diazomethane:



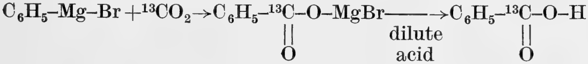
$$R\text{–}\underset{\underset{O}{\|}}{C}\text{–}Cl + 2CH_2N_2 \rightarrow R\text{–}\underset{\underset{O}{\|}}{C}\,.\,CHN_2+CH_3Cl+N_2$$

(iii) Rearrangement of the diazoketone with water in the presence of colloidal silver:



$$R\text{–}\underset{\underset{O}{\|}}{C}\text{–}CHN_2+H_2O \rightarrow R\,.\,CH_2\,.\,COOH+N_2$$

The problem to be decided is whether the carbon atom of the –COOH of the original acid becomes the carbon atom of the –COOH group of the final acid. This was demonstrated as follows: Benzoic acid containing an excess of ^{13}C in the –COOH group was prepared by reaction between phenyl magnesium bromide and carbon dioxide labelled with heavy carbon.



$$C_6H_5\text{–}Mg\text{–}Br+{}^{13}CO_2 \rightarrow C_6H_5\text{–}{}^{13}\underset{\underset{O}{\|}}{C}\text{–}O\text{–}MgBr \xrightarrow[\text{acid}]{\text{dilute}} C_6H_5\text{–}{}^{13}\underset{\underset{O}{\|}}{C}\text{–}O\text{–}H$$

After carrying out the Arndt-Eistert reaction the heavy carbon was found associated with the carboxyl group of the phenyl acetic acid formed.

$$C_6H_5\text{–}{}^{13}\underset{\underset{O}{\|}}{C}\text{–}O\text{–}H \xrightarrow[\text{Reaction}]{\text{Arndt-Eistert}} C_6H_5\text{–}CH_2\,.\,{}^{13}COOH.$$

The significance of this demonstration in connection with the mechanism of the reaction is discussed in the original paper.

Applications of ^{18}O, ^{13}C and ^{15}N to Analytical Problems.

The per cent. oxygen content of an organic compound is usually obtained by deducting the percentages of all other elements present from 100. Thus any errors in the estimations of other elements present will affect the accuracy of the estimation of the oxygen. A direct method of estimation of oxygen has recently been introduced by making use of heavy oxygen.(52)

A few milligrammes of the organic compound are burnt with a definite amount of oxygen containing a known excess of ^{18}O. The dilution of the heavy oxygen by the normal oxygen originally present in the compound is then determined. The results are then sufficient to enable the per cent. oxygen to be calculated. Using oxygen containing about 2% ^{18}O, the oxygen contents of acetic acid, formic acid, nitro-methane and diethyl ether respectively were obtained within ±3%. This accuracy is not all that might be desired, but by improving the technique or by using oxygen containing a larger proportion of ^{18}O the accuracy could be improved.

The same type of procedure has been applied to the estimation of carbon(53) and of nitrogen(54) in organic compounds. With the higher percentages of ^{13}C and ^{15}N available the estimated values showed a lower average error, namely ±0·3%.

CONCLUSION.

Although isotopic tracer work has been in progress for a comparatively short time, it may be seen from the examples considered that much has been added to our knowledge of the way in which many chemical reactions occur. In certain cases this new knowledge could not have been gained other than by the use of a separated isotope as a tracer element.

It is, perhaps, fortunate that for the elements H_2, N_2, O_2 and carbon which play such an important part in the chemistry of everyday processes the stable isotopes may now be separated by comparatively simple means as these have proved more useful as tracers than the corresponding radio-active isotopes.

The measurement of the isotopic composition of a sample of oxygen or of hydrogen is readily carried out by the accurate measurement of the density of water formed from the sample. For carbon and nitrogen, however, the measurement requires the use of a mass-spectrograph. The absence of this latter equipment, which is highly expensive, is probably the limiting factor to the uses of the heavy isotopes of carbon and of nitrogen in Australian universities. This, perhaps, is unfortunate, as these two isotopes would appear to be of particular value to the study of the mechanisms of many organic reactions.

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OCCURRENCE OF THE BRACHIOPOD GENUS *PLECTODONTA* KOZLOWSKI AT BOWNING, NEW SOUTH WALES.

By Ida A. Brown.

With Plate XIV and one text-figure.

Manuscript received, July 28, 1948. Read, September 1, 1948.

Abstract.

Small fossil brachiopods occurring in the Hume Series in the Yass-Bowning district in N.S.W. are shown to belong to the Silurian genus *Plectodonta* Kozlowski; these specimens had previously been referred by Mitchell (1923) to the Devonian genus *Stropheodonta* Hall.

Introduction.

The reported occurrence of *Stropheodonta* spp. by Mitchell (1923) from fossiliferous beds at Bowning, N.S.W., has led to doubt of the Silurian age of the rocks in which these fossils were found. On account of the awakened interest in Upper Silurian and Lower Devonian palæontology and stratigraphy by workers in New South Wales and Victoria at the present time, it has been deemed advisable to investigate the validity of Mitchell's generic identifications in the light of more recent palæontological work in other parts of the world.

I am greatly indebted to Dr. G. A. Cooper, of the U.S. National Museum, Washington, D.C., for his kindness in permitting my use of the collections under his control and for other help and advice in the study of Palæozoic brachiopods, and to Mr. H. O. Fletcher, of the Australian Museum, Sydney, for permission to re-examine Mitchell's specimens in his care.

Field Occurrence.

Mitchell's specimens come from several well-defined zones in the ***Hume Series***, a conformable series of limestones, shales and fine-grained tuffs, whose characters have been described recently (Brown, 1941, pp. 319–326).

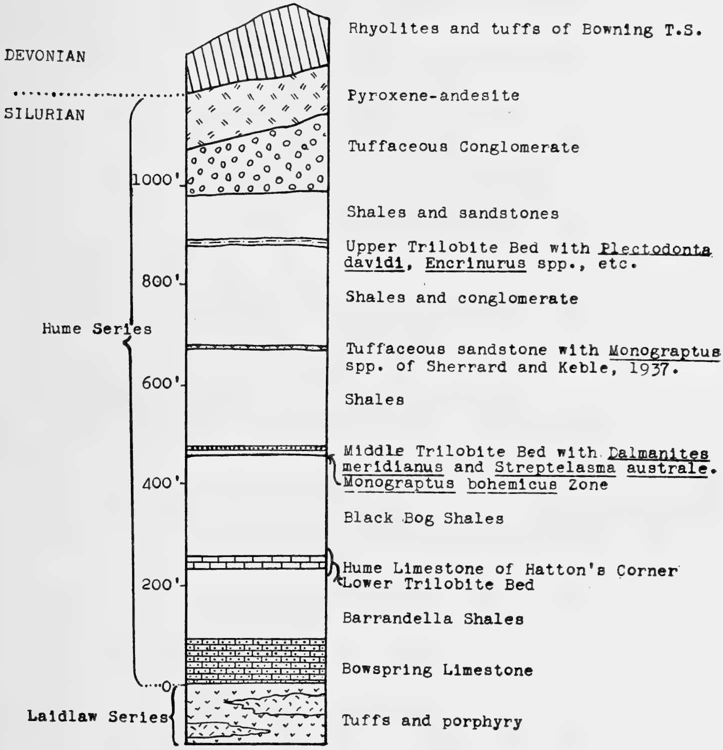
The Hume Series is the uppermost member of a sequence of Silurian sediments that have been folded into an elongated basin or synclinal structure (see map, Brown, 1941, Pls. XIV-XV).

The folded series is overlain unconformably by a series of rhyolites and acid tuffs, which outcrop mainly to the west and south of the Yass-Bowning area, although outliers occur capping several different units of the Silurian sequence on Bowning Hill and also to the south of Yass. The rhyolites and tuffs belong to a petrographic province distinct from that of the Silurian of New South Wales, and are regarded as of Devonian age. They in turn are overlain, more or less conformably, by a series of shales and thin-bedded limestone containing Devonian fossils, which crop out along the valley of the Murrumbidgee River below Taemas Bridge, and whose stratigraphy and palæontology is being investigated at the present time.

The accompanying text-figure shows diagrammatically the sequence of Silurian beds in the vicinity of Yass and Bowning.

The Hume Series is richly fossiliferous throughout its lower portions, the Bowspring limestone, Barrandella shale and Hume limestone; the overlying Hume shale is not so prolific, but does include several graptolite (***Monograptus*** spp.) horizons both above and below the Dalmanites or Middle Trilobite Bed, and the Upper Trilobite Bed occurs near the top of the series.

Mitchell was well aware of the geological sequence in the vicinity of Bowning, and his published geological section (1888) in an east-west direction through Bowning Railway Station gives a faithful representation of the order of succession of the beds, although their dips are greatly exaggerated. Mitchell's " Lower Trilobite Bed " includes the Hume limestone (with its rich coral fauna of Hatton's Corner) and the shales immediately above and below.



Text-figure A.—Diagrammatic columnar section of the Silurian sediments in the vicinity of Bowning, New South Wales. Approximate thicknesses (in feet) are indicated for the senctio between Hatton's Corner and Bowning.

The accompanying table shows the stratigraphical distribution of Mitchell's species. All but three are from the Lower Trilobite Bed and are associated with undoubted Silurian fossils, well below the *Monograptus* beds. The remaining three of Mitchell's species were found in the Upper Trilobite Bed and these are specially considered in this paper. The only known outcrop of the Upper Trilobite Bed occurs under the Goods Shed at the eastern end of Bowning Railway

Station and along a small creek immediately to the south and east. The shales show conspicuous, rather highly-inclined cleavage but the true bedding-planes dip at angles of only about ten degrees. The fossils which have been recorded from this bed are listed in the paper to which reference has been made (Brown, 1941, pp. 330–332). These include 14 species of trilobites, three of *Conularia* and three of small brachiopods, which Mitchell referred to *Stropheodonta.* The trilobites include *Encrinurus* and other genera not known above the Silurian in other parts of the world ; six of the species recorded from the Upper Trilobite Bed range upwards from lower beds. Mitchell's collections were made over the period of his twenty years' residence in the district and subsequent visits, but the collecting at most of his localities is now very poor.

Mitchell's Identifications.	Ventral Valve.	Dorsal Valve.	Geological Horizon.		
Stropheodonta bendeninensis Mitch.	×	—	L	—	—
S. silverdalensis Mitchell	×	—	L	—	—
S. borseoides Mitchell	?	×	L	—	—
S. conica Mitchell	×	—	L	—	—
S. phalœnoides Mitchell	×	?	L	—	—
S. transversa Mitchell	×	?	L	—	—
S. lilydalensis Chapman (?)	×	—	L	—	—
S. quadrata Mitchell (non Calvin, 1878)	×	—	L	—	—
S. incerta Mitchell	—	×	L	—	—
S. davidi Mitchell	×	×	—	—	U
S. minuta Mitchell	×	×	L	M (?)	—
S. bowningensis Mitchell	—	×	L	—	—
S. striato-costata Mitchell	×	×	—	—	U
S. striato-punctata Mitchell	×	—	—	—	U
S. fragilis Mitchell	×	—	L	—	—

× = valve present.
— = valve not known.
? = uncertain.

U = Upper Trilobite Bed.
M = Middle Trilobite Bed.
L = Lower Trilobite Bed.

PALÆONTOLOGY.

The specimens described in Mitchell's paper (1923) consist of internal or external moulds, usually of single valves, as indicated in the accompanying table.

In the matter of generic determination Mitchell was evidently handicapped by the paucity of his material, by lack of comparative collections and by inadequate descriptions of genotypes in other parts of the world.

In recent years studies of the Stropheodontids have been published by Stainbrook (1938, 1943, 1945), Caster (1939), Cooper (1944) and Allan (1947). It is clear from these works, and from direct comparison with specimens in the collections in the U.S. National Museum, Washington, D.C., and elsewhere, that no true Stropheodontid is present among the Bowning specimens.

Apparently Mitchell was misled by the occurrence of a denticulate hinge into placing his specimens with the Devonian genus *Stropheodonta*, for Kozlowski (1929, pp. 112–113) and others have shown that denticulation is developed in several different stocks of the brachiopods, in the Stropheodontids (*Stropheodonta*), the Chonetids (*Eodevonaria*) and the Sowerbyellids (*Eoplectodonta* and *Plectodonta*).

Examination of Mitchell's specimens in the Australian Museum, Sydney, shows that they belong to the group of Sowerbyellids, described by Jones (1928), Kozlowski (1929) and others. The Sowerbyellids range through the Ordovician and Silurian in Europe and North America but rarely, if ever, continue into the

Devonian. The early forms in the Ordovician include *Sowerbyella* Jones (s.s.); later forms, in the early Silurian, possess denticulation along less than half the hinge, as in *Eoplectodonta* Kozlowski, while some of the succeeding forms in the Wenlock and Ludlow of England and the Borszczów stage of the Silurian of Poland, develop denticulation along the greater part of the hinge, as in *Plectodonta* Kozlowski.

The Bowning specimens from the Lower Trilobite Bed appear to belong to the genus *Eoplectodonta* Kozlowski, and those of the Upper Trilobite Bed should clearly be included in *Plectodonta* Kozlowski.

With regard to specific determinations I consider that there is insufficient evidence for erecting the number of species which Mitchell proposed. Of the three species from the Upper Trilobite Bed, all of which occur at the one locality, one (*P. davidi*) is represented by two specimens of internal moulds of conjoined valves and two separate internal moulds of single valves; another species (*P. striato-costata*) is represented by a single valve and a specimen of an external mould of both valves and the third species (*P. striato-punctata*) by an external mould of a single ventral valve. I consider that the first two are probably conspecific and the third possibly also conspecific with these.

Of the rest of his material only one species (*S. minuta*) is represented with certainty by both valves, and this appears to be simply a very small immature shell. All other ten species described and figured by Mitchell come from the Lower Trilobite bed; they are all represented by moulds of single valves only and probably represent variations of but a few species. Much more material is necessary for adequate determination.

No holotypes were designated in Mitchell's publication, but the illustrated specimens are identified in his handwriting on the Australian Museum labels and the holotype chosen in the present paper is in conformity with his indication.

SYSTEMATIC DESCRIPTION.

Superfamily STROPHOMENACEA Schuchert, 1896.

Family PLECTAMBONITIDÆ O. T. Jones, 1928, emend R. Kozlowski, 1929.

Genus *Plectodonta* Kozlowski, 1929.

Genotype: *Plectodonta mariæ* R. Kozlowski, "Les Brachiopodes Gothlandiens de la Podolie Polonaise", *Palæontologia Polonica*, T.1, Warszawa, 1929, p. 114.

Small, transverse wide-hinged, concavo-convex Strophomenacea, ornamented with fine radiating costellæ. Hinge denticulate for the greater part of its length. In the ventral valve, a short median septum, bifurcating anteriorly; the dorsal valve with two pairs of septa and a trilobed cardinal process.

Distinguished from *Sowerbyella* O. T. Jones (s.s.) by the denticulate hinge.

Plectodonta davidi (Mitchell).

(Plate XIV, Figs. 1–6.)

Stropheodonta davidi Mitchell, 1923: *Proc. Linn. Soc. N.S.W.*, Vol. xlviii, Part 4, 1923, p. 470, Pl. XLI, Figs. 19, 20, 21.

S. striato-costata Mitchell: *Ibid.*, p. 472, Pl. XLII, Figs. 29, 30.

(?) *S. striato-punctata* Mitchell: *Ibid.*, p. 472, Pl. XLII, Fig. 31.

Holotype.—Aust. Mus. Coll., F.28749; Plate XIV, Fig. 1*a*.

Topotypes.—Aust. Mus. Coll., F.29383, F.28755 (internal mould of ventral valve), F.28754 (internal mould of dorsal valve).

Description.—Shell concavo-convex, semi-elliptical, small; length of holotype, 3·7 mm.; width, 6·0 mm. Other specimens are even smaller.

The holotype is an internal mould of both ventral and dorsal valves, opened out into approximately one plane. Traces of finely costellate, radiating ornamentation are indicated near the margins of the internal mould, there being 24 radiating costellæ in each valve. Shell structure pseudopunctate. The hinge is as wide as the shell. Delthyrial and notothyrial characters are somewhat obscure ; primary teeth and sockets are small and divergent, and denticulations occur along the greater part of the hinge-line, but the hinge is not holodenticulate. A short median septum in the ventral valve bifurcates anteriorly. The cardinal process has at least two lobes and appears to be fused to the brachial processes. The dorsal interior shows two strong septa extending at least two-thirds of the radius of the shell, flanked laterally by shorter septa and several radiating rows of tubercles. The muscular areas are relatively large (see Plate XIV, Figs. 1, 2). Pallial markings are not known for *P. davidi* but a specimen of *Plectodonta bendeninensis* (Mitchell) from the Lower Trilobite Bed shows the pallial markings clearly and is illustrated in Plate XIV, Fig. 7.

Geological Horizon.—Upper Trilobite Bed, Hume Series.

Locality.—Bowning Railway Station, N.S.W. Coll. J. Mitchell.

Discussion.—The Bowning specimens closely resemble one (No. 84344) in the U.S. National Museum, Washington, D.C., of *Plectodonta mariæ* Kozlowski from the Borszczów stage of the Silurian of Uścia Biskupie-Chudykowce, Poland, identified and presented by R. Kozlowski. A photograph of the latter specimen, kindly taken by Dr. G. A. Cooper, is reproduced on Plate XIV, Figs. 8 and 9, for comparison with the Bowning specimens.

There are also resemblances to other specimens in the U.S. National Museum and Sydney University collections of *Leptæna transversalis* Dalm (pars.), which has been referred by later authors to *Plectambonites*, *Sowerbyella* or *Plectodonta* (see O. Holtedahl, 1915 ; O. T. Jones, 1928, pp. 509–511 ; and Cooper, 1944, p. 335). These specimens come from various localities in the lower Gothlandian of Gotland ; the Upper Llandovery beds of River Severn, Wales ; the Wenlock Shales of Dudley, England ; and from the Silurian of North America. Some of these specimens, whilst showing all of the other essential characters of *Plectodonta*, possess a hinge with denticulations along only half the length of the cardinal border, and by Kozlowski's definition should therefore be referred to his genus *Eoplectodonta*. The majority of these specimens have ventral valves that are more convex than those of the species from the Upper Trilobite Bed of Bowning.

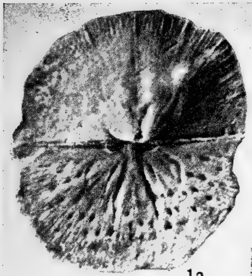
Geological Age.

The stratigraphical evidence at Bowning indicates that the Upper Trilobite Bed containing *Plectodonta davidi* (Mitchell) is closely related to the underlying Silurian sediments and is separated from the Devonian beds by a major structural break.

The species most like *P. davidi* occurs in the Polish sequence, the Borszczów stage of the Gothlandian, correlated by various authors either with the top of the Lower Ludlow or within the Upper Ludlow of the English succession (see Kozlowski, 1929, p. 23).

The partially denticulate *Sowerbyella* and *Eoplectodonta* come from the Ordovician or the lower part of the Silurian of Europe and North America.

Thus *Plectodonta davidi* (Mitchell) (hitherto referred to the genus *Stropheodonta*) confirms the evidence of the associated fauna of the Upper Silurian (possibly Ludlow) age of the Upper Trilobite Bed at Bowning, N.S.W.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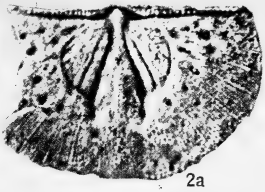
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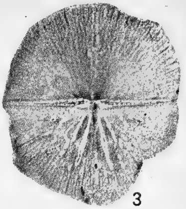
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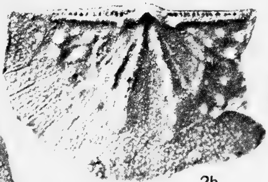
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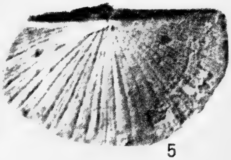
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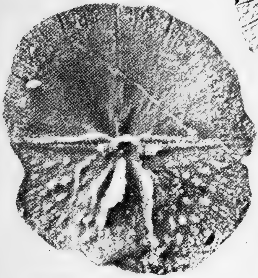
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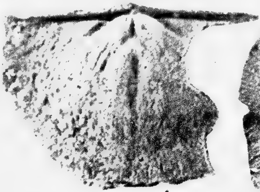
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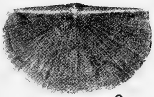
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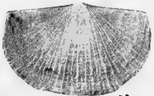
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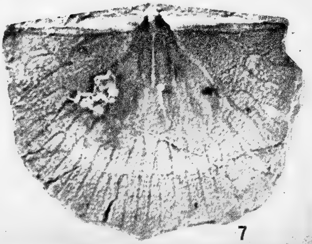
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EXPLANATION OF PLATE XIV.

All photographs are from untouched negatives; specimens were coated with ammonium chloride. Specimens figured 1 to 6 are all from the Upper Trilobite Bed at Bowning, and are now in the Australian Museum, Sydney.

Figs. 1-4.—*Plectodonta davidi* (Mitchell).

1*a*. Holotype, F.28749. A natural internal mould of both valves. Mag. ×6. Photo I.A.B.

1*b*. A rubber cast taken from the holotype (Fig. 1*a*) to show internal characters of both valves. Mag. ×6. Photo I.A.B.

2*a*. Topotype, F.28745. A natural internal mould of a dorsal valve. Mag. ×6. Photo I.A.B.

2*b*. A rubber cast of specimen (Fig. 2*a*) showing the internal structures of the dorsal valve; cardinal process fused to the brachial processes, denticulate hinge, two pairs of septa, large adductor scar areas and radial ornamentation. Mag. ×6. Photo I.A.B.

3. Rubber mould of topotype, F.29383. Conjoined valves similar to the holotype. Mag. ×6. Photo G. A. Cooper.

4. Topotype, F.28755. A natural internal mould of the ventral valve, showing bifurcating median septum. Mag. ×6. Photo I.A.B.

Figs. 5-6.—*Plectodonta davidi* (Mitchell) (=*Stropheodonta striato-costata* Mitchell).

5. Topotype, F.28748. A natural external cast of a dorsal valve. Mag. ×6. Photo I.A.B.

6. Topotype, F.28750. A natural external cast of conjoined valves. Mag. ×6. Photo I.A.B.

Fig. 7.—*Plectodonta bendeninsis* (Mitchell).

7. Loc. Lower Trilobite Bed near Bendenine Public School. A rubber mould of F.28788 (Aust. Mus,), A ventral valve showing pallial markings. Mag. ×3. Photo I.A.B.

Figs. 8-9.—*Plectodonta mariœ* Kozlowski, 1929 (84344, U.S.N.M. Coll.).

Loc. Uscie Biskupie-Chudykowce, Poland. Silurian (Borszczów Stage).

8. Portion of slab of rock showing complete specimens and internal of dorsal valve. Mag. ×2⅓ Photo G. A. Cooper.

9*a*. Dorsal view and 9*b* ventral view of complete specimen showing external ornamentation. Mag. ×2⅓. Photo G. A. Cooper.

STRUCTURAL DATA FOR THE NORTHERN END OF THE STROUD–GLOUCESTER TROUGH.

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With Plate XV and two text-figures.

Manuscript received, June 20, 1948. Read, September 1, 1948.

CONTENTS.

INTRODUCTION AND PREVIOUS INVESTIGATIONS.

The Stroud-Gloucester Trough is one of the larger tectonic features of N.S.W., extending from the coastal country east of Raymond Terrace more or less meridionally to the latitude of Gloucester—a distance longitudinally through the Trough of about 65 miles. The main synclinal structure has been known to geologists for about one hundred years, as it is developed in country which was amongst the earliest to be settled in N.S.W., having been put to pastoral and mining use by the notable Australian Agricultural Company, which employed geologists and engineers to investigate the natural resources of its properties.

On account of the discovery of Permian coal eight miles to the north of Stroud, and later in the region between Stroud and Gloucester, considerable exploration was carried out in the country concerned, and it was early known to geologists that the coal measures were developed in a main basin twenty-five miles long (and possibly in a subsidiary basin) constituting the central part of the Trough, whose bounding structure was a double series of volcanic ridges, one series on the east and the other on the west.

F. Odernheimer described many salient features of the Basin in his Reports on the Geology and Mineralogy of the A.A. Co.'s Port Stephens Property (1855–1857). Later investigations by officers of the N.S.W. Mines Department (J. Mackenzie, 1875 ; T. W. E. David, 1887) extended knowledge of the Trough, and in 1907 Professor David described the Coal Basin between Ward's River and Stroud. Several further small reports appeared in the Reports of the Mines Department and in Jaquet's Memoir on the Iron Ore Deposits of N.S.W. (1901) reference to the earlier work was given.

It may fairly be said that no detailed work was done upon the northern part of the Trough until 1921, when C. A. Sussmilch described the general geology of the Gloucester District and discussed several interesting problems of the stratigraphy and structure of the Palæozoic rocks.

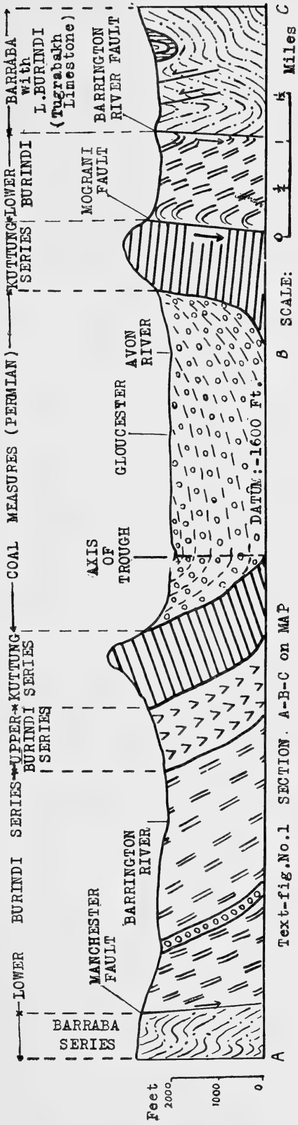
Sussmilch established the general Carboniferous sequence, and dealt with the relationships of this system to the Devonian and Permian Series, respectively. He was strongly of the opinion that the Devonian and Carboniferous were separated by an unconformity. He considered that the Coal Measures in the district were of Upper Permo-Carboniferous (Permian) age, and had been folded harmonically with the underlying Carboniferous, although a strong disconformity existed between the two groups. He emphasized the fact that the strong resistant lavas of the Kuttung Series made rugged ridges which were in great contrast with the subdued and low-lying topography of the central area given over the the Coal Measures.

To account for the behaviour of the outcrops of Palæozoic units, Sussmilch postulated and showed on his map a number of fairly powerful faults. While he considered these necessary to explain the structural features, he did not describe them, nor did he critically examine the zones of shatter.

In later years A. H. Voisey (1940) paid considerable attention to the area, particularly regarding the stratigraphy, and has made an important contribution. This may be said to have amplified and to some extent to have superseded the stratigraphical details given by Carey and Browne (1938) in an important paper summarizing the tectonics and other aspects of the Carboniferous System in eastern Australia.

Voisey, however, in his map, gave an imperfect picture of the structural relations of the region, but it must be pointed out that he was not vitally concerned with the tectonic problems.

In 1929 Osborne (see Bibliography) referred to the Stroud-Gloucester Trough when tracing the evolution of the trend-lines in the Hunter-Manning region, and



Text-fig.No.1 SECTION. A-B-C on MAP

regarded the initial downwarping of the syncline as the earliest phase in the Late Palæozoic (now called the Hunter-Bowen) orogeny (see 1929, pp. 456, 458, 460). In a later paper (1938), dealing with the southern end of the Trough, Osborne established some relations between two periods of faulting and the genesis of the Trough, and confirmed the earlier (1929) opinions and gave some details of the evolution of the Trough in its middle and southern portions.

In 1933, 1937 and more recent years, Osborne has spent considerable time mapping several features of the Gloucester-Rawdon Vale and Stroud areas, having noted and named the Rawdon Vale and Girvan Anticlines and the Waukivory Structure which flank the Trough on either side.

Faults postulated by Sussmilch, and minor structures in the Coal Measures of Weistmantels and Ward's River (in the central part of the Trough) were measured and these revealed that the Coal Series had suffered much more strongly than the Carboniferous lavas during the Upper Palæozoic orogeny.

A considerable amount of stratigraphical work was also done in the Gloucester-Chichester-Monkerai region, but less attention was paid to the eastern side of the Trough. The researches of Voisey have made it unnecessary to pursue the study of the Carboniferous stratigraphy on the western side of the Gloucester area to any great extent, but the relations of this western segment to the areas lying directly southward are being investigated at the present time.

In 1947 P. B. Andrews devoted a considerable amount of time to a study of the Stratford-Gloucester district, paying most attention to the structural aspects, but also recording stratigraphical and physiographical data. A forthcoming paper will make available the results of his work in these last-mentioned branches, especially with regard to the eastern side of the Trough in this province.

The present paper is for the purpose of recording data pertinent to the tectonic study of the Trough, and represents a summation of observations over a long period by Osborne, and a recent intensive study by Andrews. The evolutionary aspects of the Trough's history in the Structural Plan of the Hunter-Manning-Myall Province is at present under preparation by the senior author, and these special aspects will not be traversed here. The map accompanying this paper has been prepared by Andrews. It incorporates more accurate mapping than has been done hitherto in the area. The study of the small-scale structures near Craven (which match those studied by Osborne further south) is the work of Andrews.

General Shape of the Trough.

As shown in the section (Text-figure 1), the Trough is marked by steep dips on both sides and an asymmetry which helps to produce such a wide alluviation of the valley excavated between the lines of meridional Carboniferous highlands. This asymmetry is clear from a study of the dips (see map), especially in cross sections such as that available from detailed examination of outcrops near the Buckets Road in the neighbourhood of the Gloucester River. It seems clear to the authors that the Coal Measures are mostly in normal contact with the Carboniferous floor, although disconformable in several places. They do not appear to be faulted against the resistant Carboniferous margins of the Trough, in the northern sector. However, faulted junctions do occur further south.

The axis of the Trough is decidedly to the west of the central geographic plane of the structure, and lies more or less along the course of the Gloucester River. Little can be found out regarding the plunge of the axis, but it is clear from the southward dips in the environs of the town of Gloucester that the northern part of the Trough is marked by a notable southward pitch. We must not overlook, however, the effect of the Barrington River Fault which throws to the south and shuts off the Basin on the northern margin. It is interesting to note that Odernheimer recorded the southerly plunge, basing his opinion on the examination of dips west and north of Gloucester.

The Trough is bordered, east and west, by powerful faults which are parallel to the significant lines of strike of the major fold. One of us (G.D.O.) has given evidence of the probable early relationship of these faults to the major fold in the Trough.

FAULTS.

General.

These may be divided readily into major and minor groups. Many of the latter are associated with the small-scale crumpling of the Coal Measures, while some are genetically related to certain of the major fractures.

The major set are again divisible into

(*a*) Meridional faults cognate with the early Trough-fold.

(*b*) Approximately east-west faults younger in age than (*a*).

Studies of small-scale fractures in quarries and elsewhere (many of which are results of the earlier survey) have been used as pointers to the tectonic environment existing in the larger areas of the Trough. These minor structures show a great contrast in evolutionary character. The following brief statements indicate the types of strain and fracture-pattern which occur in diverse manner through the brittle rocks examined:

(*a*) Compression joints associated with small thrust faults have been observed striking within the interval N.N.W.-N.W. and dipping at moderate or low angles to both N.E. and S.W.

(*b*) Closely packed tension joints, sympathetic with steep normal faults, mostly trending north and south, or at a small angle thereto.

(*c*) High angle shear-joints in systems were measured in the earlier survey in the area between two of the larger east-west faults. These point to two possible alternatives for the origin of the larger faults (see below).

(*d*) Slickensides on almost vertical planes bordering normal faults point to a movement along them at a time subsequent to the original faulting.

Description of the Faults.

Major Group. (a) Those with a N.-S., N.N.W. or N.N.E. Strike.

The Manchester Fault. This fracture is revealed by close study of the country between the Rawdon Vale Road near Faulklands in the south and the Copeland Road in the north. Exposures a little north of the Berrico Road, between it and the Gloucester River, show the Barraba and Lower Burindi strata standing almost vertically and hading slightly to the west. Many joints run parallel to the fault, which is normal with downthrow to the east. The basal part of the Lower Burindi hereabouts contains a notable conglomerate horizon, and the fault has thrown the Burindi Series to the east and exposed—west of the fault—a low zone in the Barraba mudstones. On the Copeland Road the same type of jointing is seen.

The fault is responsible for the juxtaposition of the Lower Burindi and Barraba Series along the western sector of the Trough. The fault has considerable displacement but its geometrical features are not known. The possibility of this Manchester Fault being the northward continuation of the Williams River Fault (Osborne, 1938) must be considered.

The East Stratford Fault. This dislocation has a swinging strike and cuts obliquely across the Kuttung and Burindi strata on the east side of the Trough, about 4½ miles from Stratford. The associated joints in this zone suggest that this fault is intimately related to the main synclinal structures, thus being a truly strike fault.

In summary, therefore, we note that the two bounding faults of the Trough are probably due to stress-relief following the early compression that produced the meridional fold-structure. After severe compression the rocks opened up in a period of tension which followed the overstraining of the area.

Minor Faults and Those of Intermediate Magnitude.

Osborne has measured several small faults which fall into one of the two following categories:

(*a*) Those due to stress-adjustment after initial folding.

(*b*) Those due to shearing as a result of the early compression.

Of those to be placed in group (*a*) we have to record several fractures to be seen in the Faulklands-Berrico sector. Under (*b*) we should probably record the fractures noted by Sussmilch at the northern end of the Trough and re-studied by Andrews and named by him the *Bowman Road Fault* and the *Kiaora Fault.* The former is related to a small thrust west of it, which thrust dips westerly as seen in a cutting on the Barrington Road. The latter is probably a thrust which is responsible for the eastern boundary of the sunken block of Permian Coal Measures.

The Bowman Road Fault can be followed from the Bowman River bridge to Portions 16 and 417, A.A. Co.'s Grant, where it truncates the well-known outcrop of the Gloucester Buckets volcanic series, where these rocks are beginning to thin a little and to take on an east-west strike.

The Kiaora Fault is complementary to the Bowman Road Fault, and like the latter has been cut off by the Barrington River Fault. The effect of these faults and erosion upon the downthrown block of Permian Coal Measures has been to produce a lateral shift of about 1½ miles northward.

An inferred fault, of steep dip, which has not been named, is shown on the map, striking a little north of west, and lying to the east of the Tugrabakh Road, northward from its junction with the Krambach Road. This probable fault would explain the association of steeply dipping Middle Devonian (Tamworth) Series on the Tugrabakh Road, and Barraba mudstones and tuffs in the country immediately east of the road. These mudstones, which underlie the Tugrabakh limestone, are well exposed in the quarry beside the road junction. This fault would probably dip strongly to the east.

East-West System of Faults.

Sussmilch postulated the probable existence of a branched fault-system trending roughly east and west through a zone four miles long and lying about a mile north of Gloucester. This was regarded by him as a major dislocation-zone because it truncated the Trough and placed it against a Devonian terrain with strike utterly opposed to the meridional trend of the synclinal structure.

The present authors have examined this fault zone closely and independently, and Andrews has been able to map the fractures more accurately than shown hitherto, and to extend the main fault to the west. The two component fracture-surfaces are here named the Barrington River Fault and the Mograni Fault.

The Barrington River Fault. This is the master fault of the east-west system, and it truncates the northerly striking Bowman Road Fault and the Kiaora Fault. Its effects are seen on the Giro Road (Portion 77, Parish of Fitzroy), where it places Lower Burindi rocks against the Devonian strata, and thence it runs east and later south-east to the confluence of the Gloucester and Barrington Rivers, from which point it swings to an easterly strike again and separates (in this neighbourhood) Upper Kuttung on the south from Middle Devonian on the north. After crossing the railway line the fault is found placing

Tamworth Beds against the Lower Burindi (this being partly due to the Mograni Fault). Further east the fault brings Barraba Series again adjacent to Lower Burindi (which are on the southern side).

The quarry at the junction of the Krambach and Tugrabakh roads gives eloquent testimony of the intensity of stress that was operative in the formation of the Barrington River Fault. The rocks are practically vertical and severely jointed, and in places cut by minor faults.

Further east, for about five miles along the course of the fault, there is a general condition of very steep strata constituting small fractured " schuppen " with erratic orientation, caught between the marginal surfaces of the fault zone. Strata to the north of the fault are of Barraba age, dipping about N. 55 E. until meeting the " schuppen " zone, where more easterly strikes prevail. Strata south of the fault are of Lower Burindi age and dip steeply to the N.N.W. The segment of Lower Burindi rocks caught between the Barrington River Fault and the Mograni Fault shows much fracturing and some conjugate shear-joints.

Mograni Fault. This is best interpreted as a branch fault, as its individuality is lost at a point one-third of a mile east of the railway line (see map). From this point the trend of the fault is first E.S.E. and then S.E. This fault makes a clear-cut boundary to the Kuttung volcanic Series which are found curving northwestward to help closure of the Trough on the eastern side. The eastern course of the fault is confirmed by the behaviour of the strata exposed in a quarry near the Krambach Road at the foot of the Brushy Cutting.

North of the fault are Lower Burindi strata with dip to the N.W., while to the south a succession of Kuttung, Upper Burindi and Lower Burindi terrains is sliced off by the fault, these series varying in strikes which reflect again the curvature of the eastern side of the Trough.

In 1933 Osborne measured the section through the Mograni Cutting and found evidence of lateral movement along small steep fractures running more or less east-west. The relation of these to the dip of the flow-planes in the rhyolites indicated slipping of the small segments westerly, parallel to the Mograni Fault.

Faults of Medium Magnitude.

The Upper Avon Fault and a Probable Fault South of Cut Hill Road. In a zone three miles wide, about the latitude of Stratford and west of that village, the continuation of the western side of the Trough is interrupted by a change in strike and the presence of the Upper Avon Fault and a possible fault running through the volcanic ridges a little south of the Cut Hill Road.

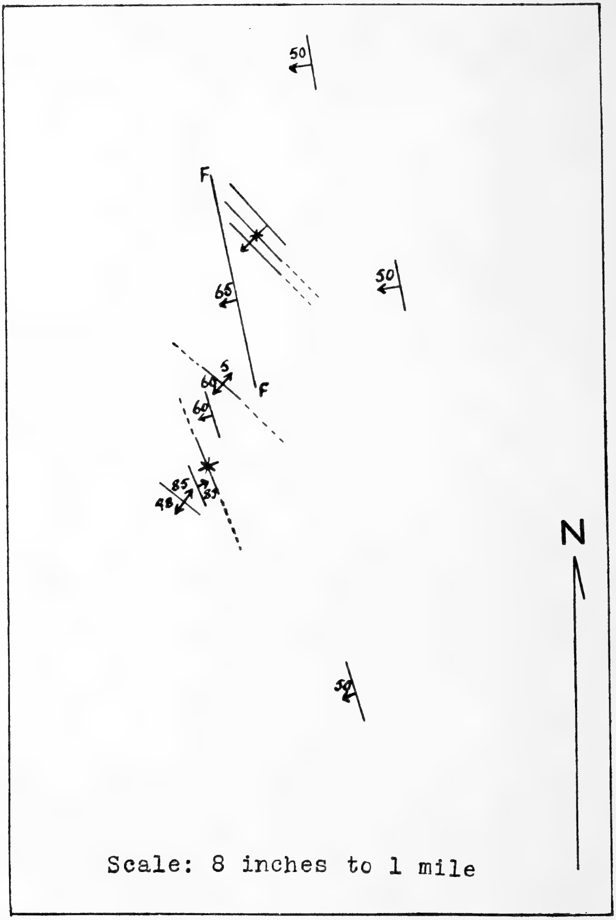
The latter fault appears to be present because of the truncation of outcrops (see map), but the authors have not been able to prove its existence to their entire satisfaction.

A bend in the strike of the west-side of the Trough from the usual meridional direction to approximately S.W. is related to movement of the west Stratford Block lying north of the Upper Avon Fault, which must have taken place during the later orogenic episode of the Upper Palæozoic diastrophism. This would give relief to other contiguous parts of the Trough, by the establishment of cross-faults.

In several parts of the area, and particularly in the district between the Turgabakh Road and the Barrington River, the Devonian strata are very intensely jointed, and most of the dips are unreliable. Careful consideration of the possible structural relations of the rocks is hampered by the ubiquitous steep (mostly vertical) and erratically trending strata.

Relations between the More Important Faults.

The two systems of faults present in the area seem susceptible of satisfactory interpretation when the course of the Hunter Bowen orogeny is considered. One of us (G.D.O.) has dealt with some aspects of this problem.



Text-fig. 2. Minor Folding near Craven

The Barrington-Mograni Fault System has truncated the Bowman Road and Kiaora Faults (N.-S. system) and thus is of later development. These faults in the north of the district are cognate with the Upper Avon and associated fractures farther to the south. The southern group, and possibly the master faults to the north, may be along zones of shear associated genetically with the compression from the N.E. which assailed the Trough in the second phase of the deformation.

The whole genetic analysis and the evolution of the complete Trough are being considered by Osborne in the preparation of a monograph at the present time, and no further discussion is intended here, especially also since critical observations have yet to be made in the central sector of the Trough.

Minor Folding near Craven.

The paucity of continuous outcrops in the Permian areas has made it difficult to map small folds, or to trace horizons in the Coal Measures. However, by means of railway and road cuttings, shafts and odd natural sections, a good deal of information that bears on the problems of the sequence of movements in the Trough is being assembled. Osborne has recently measured drag-folds and minor corrugations in the Ward's River sector.

Andrews, however, has made a special study of small-scale structure in the neighbourhood of Craven (see Text-figure 2).

Detail of Structures.

The railway cuttings between Spring Creek and Craven reveal a number of interesting minor folds in the Coal Measures. At Spring Creek and along the Pacific Highway, about one-quarter of a mile east of the railway, the strata strike meridionally and dip at 50 degrees to the west. This is also the dip in Coal Creek, close to Craven Railway Station.

Along the railway line, however, about three-quarters of a mile north of Spring Creek, the strata are seen to strike N.W. and to dip S.W. at 48 degrees. Just north of this first exposure an anticlinal axis appears, the strata to the north dipping E.N.E. at 85 degrees.

The dip of W.S.W. at 60 degrees in the next cutting north implies a synclinal axis between the two exposures. Farther north still there is another anticlinal axis.

In the cutting half a mile south of Craven Station there is a thrust fault dipping W. 10 S. at 60 degrees, causing drag-effects in the strata.

Immediately north of this fault is an anticlinal axis, striking N. 40 W. and plunging steeply to the N.W. Another 100 yards brings us to a similarly plunging syncline, which possesses drag-folds with axes parallel to the parent structure.

The fold axes described above are not parallel but trend within an interval of about 30 degrees, and intimate knowledge of neighbouring district shows that they are very local in development. They are interpreted as incompetent folds in weak Coal Measures within the major Trough-structure, and were caused by the pressure from the north-east.

Conclusion.

The descriptions given in this paper constitute a record of data obtained over a period of years by intermittent geological investigations by one of us, and by a recent intensive field-season by the other.

The evaluation of the various structural entities as criteria useful in diagnosing the evolutionary characteristics achieved by the Late Palæozoic Orogenic Episodes has only been attempted in a preliminary way. Further research along these lines and the placing of the Stroud-Gloucester Trough in the larger setting of the Hunter-Karuah province and its structural history are pressing problems now being prosecuted towards completion by Osborne.

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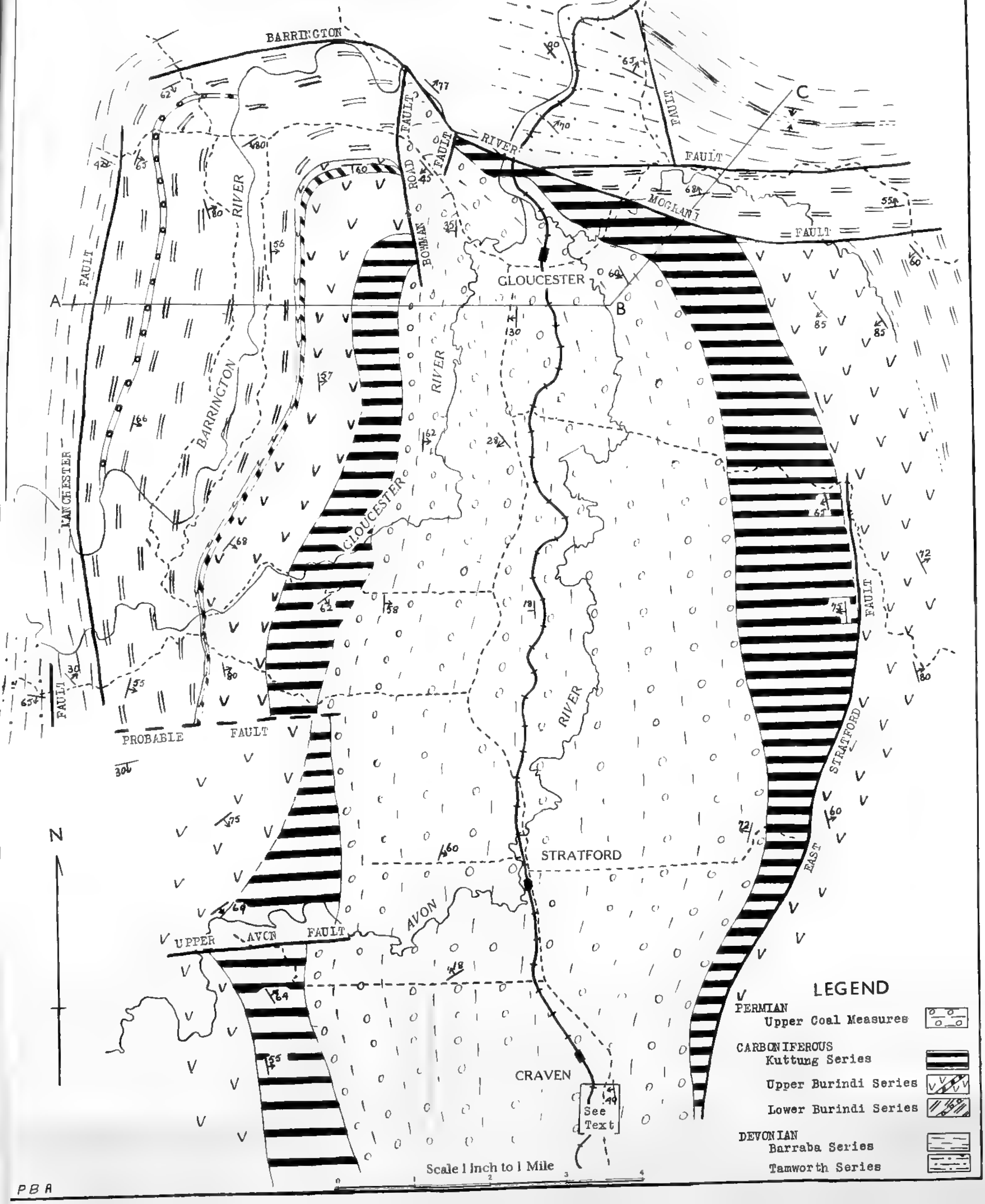
P.

GEOLOGICAL MAP
of the
GLOUCESTER – STRATFORD DISTRICT



THE CONCEPTS OF RESISTANCE, CAPACITANCE AND INDUCTANCE IN THERMAL CIRCUITS.

By R. C. L. Bosworth, Ph.D., D.Sc., F.Inst.P.

Manuscript received, October 20, 1947. Read, September 1, 1948.

Introduction.

The analogy between the flow of heat under a temperature difference and the passage of an electric current under a potential difference is widely used as a teaching aid both to elementary students in physics and in the instruction, at a slightly more advanced stage, of chemical engineering students in aspects of heat transfer phenomena. Many examples of such a treatment could be found in such a standard reference book as McAdams (1942). The analogy has been given a quantitative significance by the definition of units of thermal current and thus of thermal resistance. Harper (1928) has proposed the name " fourier " for a unit of thermal resistance and White (1938) has defined a " thermal ohm " as that unit of thermal resistance which allows one watt of heat energy flow to be generated by a potential difference of one degree centigrade.

This analogy between electrical and thermal circuits has been made the basis of a model method of studying heat flow problems by the construction of equivalent electrical circuits. Langmuir, Adams and Meikle (1913) proposed such a method some thirty years ago, and it has since been developed to deal with transients as well as steady state flow. The principal authors concerned with this development have been Beukin (1937, 1938) and Paschkis (Paschkis and Beukin, 1938 ; Avrami and Paschkis, 1942 ; Paschkis and Baker, 1942 ; Paschkis and Heisler, 1946), and their method has been primarily concerned with the flow of heat in solid insulators. Since, as they claim, oscillatory phenomena are not observed in these heat flow problems, the thermal circuits are non-inductive and may be represented by electrical models consisting of resistances and capacitances. In heat flow through a continuous block of matter the resistances branch out in all directions and thermal capacities are distributed along the resistances. In the method of Paschkis and his co-workers the body in question is broken up into a number of sections, the resistances lumped between these sections along the co-ordinate axes and the capacitances to earth concentrated at the centres of each section. Even with a limited number of sections Paschkis has claimed considerable accuracy for models of this nature.

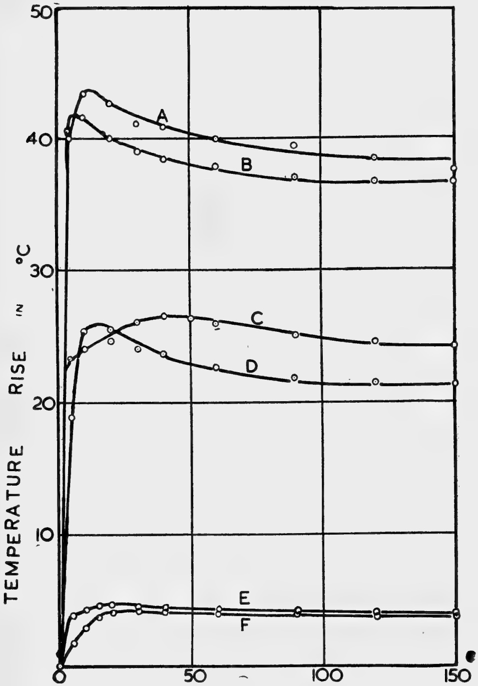
The Inductance of Natural Convection Currents.

An electric current flowing in any circuit is always associated with a magnetic field around that circuit. This field possesses a kinetic energy which has been " borrowed " from that of the electric current and as a result the electric current does not settle down immediately to a steady value if the e.m.f. is suddenly changed. That property of an electric circuit which measures the quantity of kinetic energy in the magnetic field associated with unit current is referred to as the (self) inductance of the (electric) circuit. The author (Bosworth, 1946) has claimed that the thermal circuits associated with the heat loss by natural convection in fluids show a property which could be called thermal (self) inductance. The process of heat flow sets up pressure differences which results in a flow of fluid as a convection current. The fluid flowing in the natural convection circuit possesses (mechanical) kinetic energy which has its origin in the energy of the thermal potential or temperature difference producing the heat flow. This kinetic energy bestows on the thermal circuit inductive properties. A method of demonstrating this property has been described. A device is set up capable simultaneously of measuring the heat flow from a body immersed in a fluid and the temperature difference between the surface of the body and a representative point in the fluid. At a stated time heat is suddenly supplied to the body at a steady rate and the temperature difference between the body and the fluid is measured as a function of the time giving a curve which is that of a thermal transient.

The apparatus which has been used for measurements of this nature consists of a short wire of resistance alloy, such as nichrome or constantan, to the centre of which is welded a sensitive thermocouple of fine wire. The other junction of the thermocouple is immersed in the fluid some 5 mms. from the surface of the alloy wire ; so that the couple thus measures the temperature difference between the alloy wire and some point in the fluid. The alloy wire could be heated by an electric current. Since the wire was chosen to be of material of low temperature coefficient of resistance, the heat input may be taken as proportional to the square of the heating current. The temperature difference may likewise be taken as proportional to the reading of a galvanometer attached to the thermocouple. The theory of the use of instruments of this nature has been discussed by the author (Bosworth, 1944). A.C. is preferably used for the heating current as possible errors arising from electrolysis or from an unsymmetrical welding of the thermocouple elements are thus avoided.

If such an instrument is immersed in a fluid and at a time $t=0$ a current I is suddenly applied and the readings of the temperature difference (θ) are taken at intervals, the θ versus t plot takes a characteristic form. θ rises from zero at $t=0$ to a maximum value and then falls asymptotically to the final steady value from above. Figure 1 gives some illustrative curves for the transients from a 19 gauge S.W.G. nichrome IV wire. Curve A refers to a heating current of 12·6 amps. in toluene, curve B 12·6 amps. in ethanol, curve C 7·8 amps. in carbon tetrachloride, curve D 18·6 amps. in water, curve E 4·0 amps. in toluene, and curve F 2·5 amps. in carbon tetrachloride. Interpretation of these curves is easy. The system of convection currents possess inertia and take time to settle down to the final value. The rate of heat loss for a given temperature difference is less in the absence of the full convection current, and so with a given heat input the surface initially rises to a temperature higher than that attained when a steady convection flows past the hot wire. Curves similar to those shown in Figure 1 have been recorded in a letter to *Nature* (Bosworth, 1946). It is clear that this phenomenon means that in any attempt to represent heat flow phenomena in fluids by the Paschkis method of electric models the circuits must now involve inductances as well as capacitances and resistances.

Having found systems which show heat flow phenomena which can be described as *thermal self inductance*, the obvious next step would be to attempt to describe a system showing *thermal mutual inductance*. Suppose we take two wires welded to thermocouples and place them in a fluid in such a position that the convection current from one passes over the other. The wires, considered as heat circuits, are now linked by the inductive element, the convection current. Any change in the heat flow from one hot wire will alter the magnitude of the convection current and this will change the heat flow from the other wire. We regard the heat flowing from a hot wire to the fluid as proportional to the *thermal current* and the temperature difference as the thermal p.d. or the *thermomotive* *force.* If A and B are two wires coupled by the same convection current, we may say that the system possesses the property of thermal mutual inductance if when the thermal current from A to the fluid is suddenly changed there is a transient change in the thermomotive force, or temperature difference, between B and the fluid. This property may be readily demonstrated. The following equipment was used in the demonstration.



TIME (Mins.)
Fig. 1.

Two parallel wires of 22 gauge (S.W.G.) nichrome IV each attached to a fine copper-constantan thermocouple were set, one wire vertically above the other, in a fluid. The distance apart in the first experiments was 18 mms. and the first fluid used was distilled water. A heating current of 2·0 amps. was suddenly switched on to the lower wire, causing its temperature to rise by 10·5° C., the temperature settling down to the final steady value within the period of swing of the galvanometer. The behaviour of the temperature difference between wire B and the fluid is represented by curve A in Figure 2. It will be observed that for a period of the order of a minute there is no change and then the temperature difference commences to rise, passes through a maximum of 0·52° C. in 200 seconds and then falls slowly almost to zero again. Curve B on Figure 2 shows the effect of suddenly applying a current of 8·0 amps. to the lower filament (producing a temperature rise of 70° C. between lower filament and fluid). In this case the initial period of no temperature change in the upper filament is reduced to 20 secs. The succeeding temperature rise is far steeper, the maximum of 4·6° C. being attained in 55 seconds. The return of θ to the final value was also more rapid in this case.

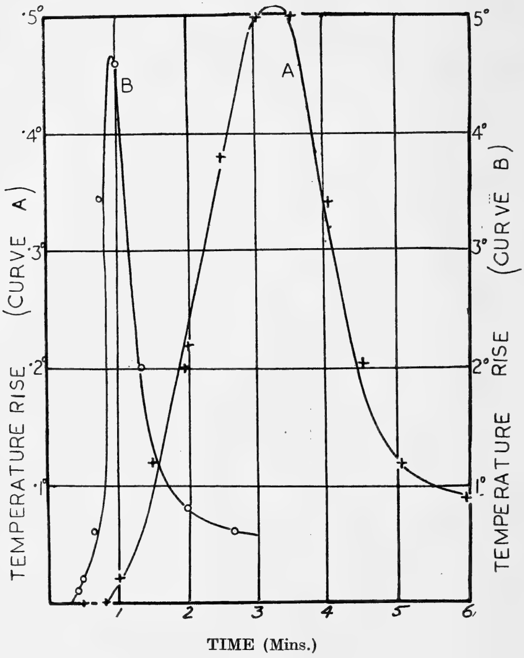


Fig. 2.

Transients of a considerably longer period are exhibited if the two filaments are immersed in a more viscous fluid. Figure 3 shows results obtained in a 75·2% sucrose solution at room temperature. The density of this solution was 1·3808 grammes per ml. and the viscosity 360 centipoises. Curve A refers to a heating current of 2·0 amps. producing a temperature rise of 43° C. in the lower wire and curve B to a heating current of 5·0 amps. producing a temperature rise of 140° C. in the lower filament. The transient thermal current induced in the upper filament has a much longer period in the former case. As far as these and similar experiments go then, the period of the transient is the longer the lower the primary temperature difference and the higher the viscosity of the fluid. This might have been expected, as the intensity of the convection current from any hot body in a fluid depends on the Grashof number which involve θ in the numerator and the viscosity in the denominator.

THE UNIT OF THERMAL RESISTANCE.

If we are to set up the equivalent electrical circuit to represent both the steady state and transient conditions obtained in the flow of heat in fluid systems careful thought must be given to the definition of the unit of thermal resistance. As claimed by the author (Bosworth, 1946*a*), the definitions of Harper and of White are not completely satisfactory. We may, however, proceed in the following way : We take the unit of thermomotive force as the degree centigrade and the unit of energy as the joule. Let us consider any length of a thermal circuit over which there is a temperature difference or thermal p.d. θ, and suppose that in a time dt a quantity of heat dQ (joules) flows through the circuit. Let the absolute temperature of the mid-point of the circuit be T. (θ will be assumed to be small in comparison with T). The work done by the flow of heat in the circuit follows from the second law of thermodynamics as

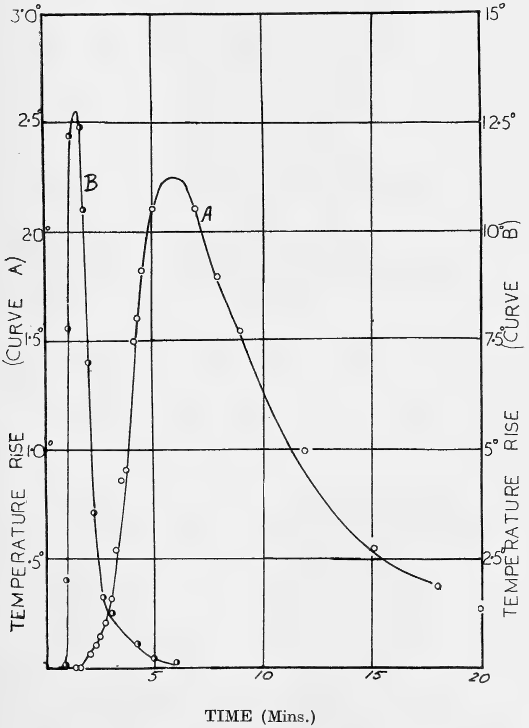


Fig. 3.

$$\frac{dQ}{T}\theta \text{ (joules).}$$

Now if I_q is the magnitude of the thermal current flowing, the work done by the current in the time dt will be

$$I_q\theta dt \text{ (joules).}$$

It therefore follows that

$$I_q=\frac{d}{dt}\left(\frac{dQ}{T}\right)=\frac{dS}{dt} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where S is the entropy gain of the sink.

If we refer to the unit of thermal current as defined by equation (1), it follows that the unit of thermal resistance, or thermal ohm, is that of a portion of a thermal circuit such that one degree centigrade produces a thermal current of one watt per degree centigrade. Consider a cylindrical conducting body of length l, cross sectional area a and of mean temperature T (degrees absolute). Let q be the quantity of heat transferred per unit area per unit time. The resistance in thermal ohms is then given by:

$$R_q=\frac{\theta T}{qa} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The specific thermal resistance, or resistivity (σ_q) of a given material may then be given by the expression

$$\sigma_q=R_q\frac{a}{l}=\frac{\theta T}{ql}=\frac{T}{q}\text{ grad }\theta \text{ or } \frac{T}{q}\text{ grad } T \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

In terms of equation (3) the specific thermal resistance of copper at 20° C. (293·1° K.) becomes

$$\sigma_q \text{ (Cu)}=75\cdot 6 \text{ thermal ohm cms.}$$

For water at the same temperature the specific thermal resistance becomes

$$\sigma_q \text{ (H}_2\text{O)}=48{,}600 \text{ thermal ohm cms.}$$

The Unit of Thermal Capacitance.

In terms of the thermal current as entropy flow and the thermomotive force as temperature difference, a definition of unit thermal capacitance may be given in the following words:

A body has a capacitance of one thermal farad if an amount of entropy of one joule per degree centigrade added to that body raises the temperature by one degree centigrade.

Thus if a body of volume V has a temperature T and consists of matter of density ρ and specific heat at constant pressure c_p, its capacitance in thermal farads (at constant pressure) is

$$C_q=\frac{V\rho c_p}{T} \text{ (thermal farads)} \quad \ldots\ldots\ldots\ldots \quad (4)$$

The capacitance of one ml. of copper at 20° C. on this basis amounts to

11·6 thermal millifarads

and of one ml. of water at the same temperature

14·3 thermal millifarads.

If a thermal capacitance C_q is charged by a thermal current I_q for a time dt, the resultant temperature rise θ is given by

$$\theta=C_q \int I_q dt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

which on substitution in equation (1) gives

$$\theta=C_q\int\frac{dQ}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

The potential energy (P) stored during this process is given by

$$\begin{aligned} P&=\tfrac{1}{2}\theta^2/C_q \\ &=\tfrac{1}{2}\theta\int\frac{dQ}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)\end{aligned}$$

which is an expression for the *available* thermal energy stored by charging the body concerned to a temperature θ above that of its surroundings.

THE UNIT OF THERMAL INDUCTANCE.

The thermal inductance of a system of convection currents may be most directly defined in terms of the temperature difference between solid surface and bulk fluid which is set up when the entropy flow is changing at a unit rate. An equivalent definition, perhaps more suitable to heat flow problems, may be expressed by the equation

$$L_q=\frac{2K_q}{I_q^2}=\frac{2K_qT^2}{(dQ/dt)^2}\text{ (thermal henries)} \quad\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

where L_q is the thermal inductance and K_q is the kinetic energy in joules stored in the system of convection currents surrounding the hot body.

The calculation of K_q for a system of known dimensions has not yet, as far as the author is aware, been effected; but should not be extremely difficult. Meanwhile, an estimate of the value of L_q may be made from the form of the thermal transient. The relaxation time for a circuit involving resistances and inductances is equal to L/R. For the systems illustrated in Figure 1 this relaxation time is of the order 10 seconds. The thermal resistance per unit length of heated wire is of the order 15,000 thermal ohms. Accordingly the thermal inductance of this arrangement of a hot wire in water is of the order of 150 thermal kilohenries.

The inductances of thermal circuits is accordingly represented by considerably larger figures than the corresponding figures in electrical circuits.

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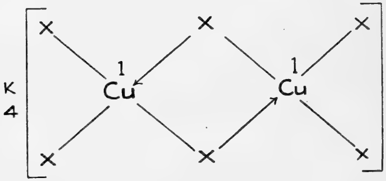
COORDINATION COMPOUNDS OF COPPER.

PART I. COMPLEX COPPER (II) CUPRATES (I).

By C. M. HARRIS.

Manuscript received September 14, 1948. Read October 6, 1948.

It is well known that copper (I) halides readily dissolve in concentrated aqueous solutions of alkali or ammonium halides, particularly on heating, to form clear solutions from which can be isolated the complex copper (I) halides $M[Cu^IX_2]$ and/or $M_2[Cu^IX_3]$ (where M=K, Na or NH_4, and X=Cl, Br or 1). The latter compounds are probably



bridged complexes as above, in which copper (I) is four covalent whilst in the other type the copper (I) atom is two covalent (Wells, 1945). Comprehensive lists of these compounds are given by Abegg (1908*a*) and Mellor (1923).

Many copper ammines are reported throughout the literature, and, amongst the ammonia compounds, tetrammine and hexammine copper (II) halides are well known. The bis-ethylene diamine copper (II) halides, $[Cu(en)_2]X_2.H_2O$ (X=Cl and Br) were prepared by Dubsky and Dostal (1932), and these together with the iodide were re-examined by Johnson and Bryant (1934) who gave evidence for the existence of the $[Cu(en)_2]^{++}$ ion in the solid state. Six covalent complexes $[Cu(en)_3]X_2$ (Dubsky *et al.*, 1932) have also been prepared and compounds of pyridine with copper (II) halides (see later) are known. Morgan and Burstall (1926) prepared the complex copper (II) dicyano cuprate (I) $[Cu^{II}(en)_2][Cu^I(CN)_2]_2$ whilst Souchay (1940) prepared the copper (II) dibromo cuprate (I) $[Cu^{II}(Pym)_2][Cu^IBr_2]_2$ with coordinated pyramidone.

In the present work a series of coordinated copper (II) dihalogen cuprates (I) containing ammonia and ethylene diamine as coordinating addenda have been prepared. The method consisted of the double decomposition of complex copper (I) halide in a concentrated solution of alkali or ammonium halide with a solution of the required copper (II) ammine also containing alkali or ammonium halide to avoid precipitation of copper (I) halide. By reacting two moles of copper (I) halide with one mole of a tetrammine copper (II) halide as above, complexes of the type $[Cu^{II}(A)_4][Cu^IX_2]_2$ have been obtained from solution as crystalline substances.

$$[Cu^{II}(A)_4]^{++}+2[Cu^IX_2] \xrightarrow{+aq.\ MX} [Cu^{II}(A)_4][Cu^IX_2]_2$$

I. $A=NH_3$; X=Cl.

II. $A=NH_3$; X=Br.

III. $A=NH_3$; X=1.

IV. 2A=en; X=Br.

V. 2A=en; X=1.

Compound I was obtained as the monohydrate if the mole ratio of copper (II) ammine to copper (I) chloride was 1 : 2 or 1 : 3 but the latter ratio was employed since it gave the best yield of product.

The ethylene diamine dichloro complex $[Cu^{II}(en)_2][Cu^{I}Cl_2]_2$ was not isolated but instead the compound $[Cu^{II}(en)_2][Cu^{I}_3Cl_5]$ was obtained. This compound is similar to the preceding compounds except that it contains an extra molecule of copper (I) chloride, and it is suggested that the extra molecule of copper (I) chloride is probably involved in the crystal lattice and the compound would be better represented as $[Cu^{II}(en)_2][Cu^{I}Cl_2]_2 . Cu^{I}Cl$ (VI). It was obtained if the mole ratio of copper (II) ammine to copper (I) chloride was 1 : 2 or 1 : 3. The latter ratio gave the best yield of the complex.

$$[Cu^{II}(en)_2]^{++}+3[Cu^{I}Cl_2] \xrightarrow{+aq.\ KCl} [Cu^{II}(en)_2][Cu^{I}Cl_2]_2 . Cu^{I}Cl+Cl^{-}.$$

It is interesting to note that a compound $4NH_4Cl . 3Cu_2Cl_2$ prepared by Wells and Hurlburt (1895) can also be formulated $(NH_4)_2[Cu^{I}_3Cl_5]$ and would appear to be the ammonium analogue of VI. Complex cyanides $R_2[Cu^{I}_3(CN)_5]$ (where $R=Rb$ and Cs and $R_2=Ca$) of similar formula to the above chloride have been prepared by Grossmann and Forst (1905).

In the compounds which are now described copper (II) exhibits its usual coordination number of four and the copper (I) atom a covalency of two, at least, in compounds I-V inclusive.

The preparation of these compounds was first attempted with the iodide III at room temperature, but owing to the large amount of potassium iodide required to prevent precipitation of the copper (I) iodide on addition to the copper (II) ammine solution it was attempted at elevated temperatures and the product isolated on cooling. This was found to be generally more successful in that it yielded a purer product and required less potassium halide in solution. The copper (II) ammine was prepared *in situ* from the corresponding copper (II) halide or in some cases diammine copper (II) acetate by adding ethylene diamine in theoretical amount or ammonia in sufficient excess to stabilize the ammine formed. The use of copper (II) sulphate for this purpose was not satisfactory as it was found to contaminate the product with potassium sulphate. Heating of the copper ammine solution was carried out in a water bath to prevent superheating of the walls of the reaction vessel and local decomposition particularly of the ammonia compounds. The complex copper (I) halide solution was always added to the copper ammine solution. Compound I was prepared at a much lower temperature using ammonium chloride instead of alkali chloride as it was found to prevent the formation of basic salts during the reaction.

A compound described as a double iodide of copper and ammonia was prepared by Saglier (1886) by treating ammoniacal copper (II) oxide with alcohol and iodine. Abegg (1908*b*) formulated the compound as III, which it undoubtedly was. The method is not as good as that now described and the product does not appear from the analytical results to have been as pure. Ritthausen (1853) claimed to have prepared a blue compound containing copper (I) and copper (II) chloride, ammonia and water. He isolated the compound as one of the products of reaction of saturated ammonium chloride solution on copper in the presence of air and assigned to it the formula $Cu_2Cl . NH_3 . CuCl . NH_3 . HO$. However it has since been postulated by Abegg (1908*b*) as $[Cu^{II}(NH_3)_4][Cu^{I}Cl_2]_2 . {}_2H_2O$. More recently Burrows and Sanford (1935) suggested that it corresponds to the formula $Cu_2Cl_3(NH_3)_3H_2O$ one of the copper atoms being in the monovalent and the other in the divalent condition and that such a compound would be analogous to the arsine derivative $[Cu_2Cl_3[(Ph_2Me)_3As]_3]^{\circ}$ described by them. The atomic ratio $Cu : Cl : NH_3$ calculated by them from R's analytical results as $1 : 1{\cdot}34 : 1{\cdot}37$ would better fit the formula $Cu_3Cl_4(NH_3)_4$ and from a consideration of its analysis, method of preparation, colour and reactions it would appear to have been the monohydrate I. The analytical results of Ritthausen's preparation are far too high for Abegg's postulated dihydrate. Compound I lost 3 per cent. of its weight on heating at 70–80° C., and this could not have been primarily due to ammonia since the ammonia content only decreased an amount equal to approximately 10 per cent. of the total loss. The compound similarly lost weight in a phosphorus pentoxide desiccator and in both cases the loss was accompanied by a colour change from violet to mauve. The loss is less than theory due to simultaneous absorption of oxygen and oxidation of copper (I) during the determination. The present method for the preparation of compound I is less ambiguous and more quantitative than that of Ritthausen.

The ammonia compound III slowly decomposes in the atmosphere, forming copper (I) iodide and liberates iodine and ammonia. The reaction proceeds to completion more rapidly on gentle heating

$$2[Cu^{II}(NH_3)_4][Cu^{I}I_2]_2 \longrightarrow 6CuI+8NH_3+I_2$$

leaving a quantitative yield of copper (I) iodide. The atmosphere above the compound in a stoppered bottle yields positive tests for iodine and ammonia. Its ethylene diamine analogue does not behave similarly, due to the fact that the chelate group, ethylene diamine, forms much more stable compounds with divalent copper than does ammonia.

On shaking vigorously with water compounds II-V are decomposed thus:

$$[Cu^{II}(A)_4][Cu^{I}X_2]_2 \xrightarrow{H_2O} [Cu(A)_4]^{++}+2X^{-}+2CuX.$$

The ammonia compounds II and III readily decompose in the cold, yielding a blue solution of the tetrammine copper (II) halide and a precipitate of copper (I) halide. The ethylene diamine compounds IV and V, particularly the latter, are more insoluble than the ammonia compounds, but decompose readily on warming, yielding a purple solution of the bis-ethylene diamine copper (II) halide and a precipitate of copper (I) halide. The tetrammine dichloro compound (I) is decomposed instantly by water to form a green insoluble basic compound. The ethylene diamine compound VI yields a purple solution of the bis-ethylene diamine copper (II) chloride and a precipitate of copper (I) chloride:

$$[Cu^{II}(en)_2][Cu^{I}Cl_2]_2 \,.\, Cu^{I}Cl \rightarrow [Cu(en)_2]^{++}+2Cl^{-}+3CuCl.$$

The compounds are all readily decomposed by dilute acids. With the diiodo compounds each molecule of the complex liberates an atom of iodine

$$2[Cu^{II}(A)_4][Cu^{I}I_2]_2+8H^{+} \rightarrow I_2+6CuI+8AH^{+}$$

with the simultaneous precipitation of copper (I) iodide, and as can be seen from the equation, each atom of iodine liberated corresponds to a molecule of divalent copper. The bromides and chlorides yield one molecule of divalent copper and a precipitate of two molecules of copper (I) halide

$$[Cu^{II}(A)_4][Cu^{I}X_2]_2+4H^{+} \rightarrow Cu^{++}+2X^{-}+4AH^{+}+2CuX,$$

except with compound VI, when three molecules of copper (I) chloride are liberated:

$$[Cu^{II}(en)_2][Cu^{I}Cl_2]_2 \,.\, Cu^{I}Cl+4H^{+} \rightarrow Cu^{++}+2Cl^{-}+2EnH_2^{++}+3CuCl.$$

In order to estimate the amount of divalent copper in the complexes an attempt was made to decompose the compounds with dilute acid in the presence of potassium iodide and to titrate the liberated iodine with sodium thiosulphate. With the diiodo compounds the decomposition of the ammonia compound was realized by shaking with dilute sulphuric acid containing potassium iodide. The ethylene diamine compound, being most insoluble, was decomposed by warming with dilute acetic acid containing potassium iodide. The chlorides and bromides were decomposed in oxygen-free solution saturated with hydrogen in the same manner as compound III, and the liberated iodine in all cases was titrated with sodium thiosulphate and the addition of ammonium thiocyanate in the usual manner. The chlorides gave varying results, although of the required order to characterize the reaction. The varying results are attributed to the ease of oxidation of the copper (I) chloride in the molecule. All the titrations were performed under conditions far from ideal in that the reactions are dependent on the interaction of a solid with a liquid phase.

The highly coloured complex copper (II) cuprates (I) are insoluble in organic solvents and decomposed by water acids and alkali, particularly on heating. The ammonia compounds are more unstable than their ethylene diamine analogues and more easily oxidized in air. The order of increasing stability to oxidation is chlorides to iodides. Silver nitrate solution is immediately reduced at room temperature to metallic silver by the monovalent copper of the anion with the simultaneous precipitation of the halogen as silver halide.

No analogous pyridine complexes could be isolated by these methods due to the immediate precipitation of blue trans-planar dipyridine copper (II) chloride (Lang, 1888; Cox, Sharatt, Wardlaw and Webster, 1936) with the chloride, green dipyridine copper (II) bromide (Pfeiffer and Pimmer, 1905) with the bromide, and black hexakis—pyridine copper (II) iodide (King, 1930) with the iodide. Although the chloride and bromide are soluble in water, they are readily precipitated again on the addition of the corresponding alkali or ammonium halide, particularly on heating, and in no way could be induced to react with the complex copper (I) halides. The iodide is insoluble in water and readily loses pyridine.

The action of boiling pyridine on the ammonia or ethylene diamine compounds also did not yield the required pyridine analogues but split the complexes forming derivatives of univalent and divalent copper. The ammonia compounds yielded a complex pyridine copper (II) halide which was precipitated by the addition of benzene and which could be filtered off, whilst the benzene-pyridine filtrate on precipitation with ether deposited a white crystalline pyridine copper (I) halide soluble in benzene from which it was purified by precipitation with ether. The ethylene diamine compounds when treated similarly leave the bis-ethylene diamine copper (II) halide section of the molecule as an insoluble precipitate, whilst the filtrate yields the pyridine copper (I) halide as before. The pyridine copper (I) chloride compound was only obtained from benzene in small amounts because it is extremely rapidly oxidized to a green substance insoluble in benzene. The pyridine copper (I) halides are insoluble in water and alcohol but soluble in benzene, and readily reduce silver nitrate to the metal with simultaneous precipitation of silver halide. They probably possess the formula $[C_5H_5N{\rightarrow}CuX]_4^{\circ}$ and would be similar to the phosphine and arsine derivatives of silver and copper (I) iodides $[R_3P{\rightarrow}MI]_4^{\circ}$ and $[R_3As{\rightarrow}MI]_4^{\circ}$ prepared by Mann, Purdie and Wells (1936). They are not very stable and the chloride and bromide are readily oxidized in air. The order of increasing stability to oxidation is chloride to iodide. The above was established qualitatively and these pyridine copper (I) halides will be investigated further at a later date.

The preparation of a similar series of compounds $[Cu^{II}(A)_4][Cu^{I}XY]_2$ containing two different halogens around each copper (I) atom of the anion has been begun with the successful isolation of tetrammine copper (II) and bis-ethylene diamine copper (II) bromo-iodo-cuprates (I). Their publication is being reserved till the complete series has been investigated.

EXPERIMENTAL.

Tetrammine Copper (II) Diïodo Cuprate (I). (III). Diammine copper (II) acetate (1·65 g. 0·0077 g. mole; Horn, 1908) in slight excess was dissolved by treating with ammonium hydroxide

(3·30 ml. of 15·0 N) followed by water (70 ml.). Added acetic acid (0·30 ml. of 17·4 N) with stirring followed by potassium iodide (20·0 g.) and when dissolved heated the solution in a water bath to 90° C. A boiling solution of copper (I) iodide (2·50 g.; 0·0131 g. mole) in water (10 ml.) containing potassium iodide (15·0 g.) was added slowly with stirring and the mixture was then cooled in ice water to 25° C. The resulting crystals were washed with 90% alcohol (25 ml.) followed by acetone (50 ml.) and air-dried as quickly as possible (tendency for compound to dissociate). This gave 4·5–4·7 g. (90–94% yield) of lustrous greenish black crystals. When the preparation was carried out at room temperature using greater quantities of potassium iodide the product was lighter in colour due to precipitation of copper (I) iodide during addition, and the ammonia content was up to 3 per cent. low. Preparations using copper sulphate in place of diammine copper (II) acetate with a smaller volume of solution and less potassium iodide gave a product contaminated with 3–5 per cent. of potassium sulphate. Hot acetone readily removes coordinated iodine and ammonia from the complex. The atmosphere above the compound in a stoppered bottle gave a blue colour with starch-iodide paper and turned red litmus paper blue, demonstrating the presence of iodine and ammonia vapours.

On heating the complex (0·3032 g.) in the oven at 105° C. to constant weight it decomposed completely to copper (I) iodide (0·2256 g.; calc., 0·2260 g.). The divalent copper in the complex was estimated from the iodine liberated by the compound on treatment with dilute sulphuric acid containing potassium iodide. The complex (1·000 g.) in a glass stoppered flask was covered with 1·5 N sulphuric acid (70 ml.) containing potassium iodide (3–5 g.). The mixture was shaken until decomposition appeared to be complete and the liberated iodine titrated with sodium thiosulphate in the usual manner, adding ammonium thiocyanate and shaking vigorously approaching the end point.

Found: Cu (total), 24·9; Cu^{++}, 8·17, 8·26; NH_3, 8·83; I, 66·2%.

Calculated for $[Cu^{II}(NH_3)_4][Cu^{I}I_2]_2$: Cu (total), 24·89; Cu^{++}, 8·30; NH_3, 8·88; I, 66·25%.

Bis-ethylene Diamine Copper (II) Diiodo Cuprate (I). (V). Anhydrous copper (II) chloride (0·82 g.; 0·0061 g. mole) was dissolved in water (25 ml.) and ethylene diamine (1·10 ml. of 69%; 0·0124 g. mole) added. Potassium iodide (5·0 g.) was then added to the stirred mixture, which was heated in a water bath to 85–90° C. To this solution was added in a fine stream with constant stirring a boiling solution of copper (I) iodide (2·33 g.; 0·0122 g. mole) in water (10 ml.) containing potassium iodide (15·0 g.). The solution containing precipitated complex was cooled in ice water with stirring to 25° C. After filtration the substance was washed with 90% alcohol (50–100 ml.) followed by acetone (50 ml.) and dried in a vacuum phosphorus pentoxide-potassium hydroxide desiccator, first removing the acetone vapours under suction. This gave 4·8 g. (96% yield) of light brown microprisms.

Owing to the compound's high insolubility the determination of liberated iodine from the divalent copper of the complex was made as follows: The complex (1·000 g.) was treated with with water (20 ml.) containing acetic acid (3 ml. of 17 N) and potassium iodide (10 g.) and heated carefully till the complex had decomposed. Cooled to room temperature, added water (40 ml.) and titrated as before.

Found: Cu (total), 23·3; Cu^{++}, 7·80; I, 61·5%.

Calculated for $[Cu^{II}(NH_2.CH_2.CH_2.NH_2)_2][Cu^{I}I_2]_2$: Cu (total), 23·30; Cu^{++}, 7·78; I, 62·01%.

Tetrammine Copper (II) Dibromo Cuprate (I). (II). Anhydrous copper (II) bromide (1·93 g.; 0·0086 g. mole) was dissolved in water (25 ml.) to which was then added with stirring acetic acid (2·0 ml. of 17·4 N) followed all at once by ammonium hydroxide (4·0 ml. of 15·0 N). Potassium bromide (2·0 g.) was added and the stirred solution heated to 80° C. in a water bath and treated slowly with a hot solution (90° C.) of freshly prepared copper (I) bromide (2·48 g.; 0·0173 g. mole) in water (15·0 ml.) containing potassium bromide (10·0 g.) and two drops of 7 N hydrobromic acid. The mixture was cooled quickly in ice water to 25° C. with stirring and the filtered complex was washed with 90% alcohol (25 ml.) followed by acetone (50 ml.). The compound was dried in a vacuum desiccator as before. The reaction gave 2·2–2·7 g. (44–54% yield) of felted slate-purple prisms. The compound is readily oxidized in moist air forming basic salts.

Found: Cu (total), 32·4, 32·6; Cu^{++}, 11·2, 11·6; NH_3, 11·7, 11·7; Br, 54·3, 54·3, 54·7%.

Calculated for $[Cu^{II}(NH_3)_4][Cu^{I}Br_2]_2$: Cu (total), 32·98; Cu^{++}, 10·99; NH_3, 11·78; Br, 55·3%.

Bis-ethylene Diamine Copper (II) Dibromo Cuprate (I) . (IV). Anhydrous copper (II) bromide (1·77 g.; 0·0079 g. mole) was dissolved in water (20 ml.) and ethylene diamine (1·40 ml. of 69%; 0·0158 g. mole) followed by potassium bromide (2·0 g.) added. Heated the stirred solution in a water bath to 85–90° C. A hot solution (100° C.) of freshly prepared copper (I) bromide (2·28 g.; 0·0159 g. mole) in water (15 ml.) containing potassium bromide (10·0 g.) and two drops of 7 N hydrobromic acid was added to the above solution in a continuous stream with stirring. The solution was cooled to 25° C. in ice water and the compound filtered, washed and dried as in previous preparation. By this method obtained 2·5–3·1 g. (50–62% yield) of lustrous dark violet prisms.

Found: Cu (total), 30·3; Cu^{++}, 9·9, 10·1; Br, 50·5%.

Calculated for $[Cu^{II}(NH_2 . CH_2 . CH_2 . NH_2)_2][Cu^{I}Br_2]_2$: Cu (total), 30·24; Cu^{++}, 10·08; Br, 50·7%.

Tetrammine Copper (II) Dichloro Cuprate (I) Monohydrate. (I). Diammine copper (II) acetate (2·69 g.; 0·0125 g. mole) was treated with ammonium hydroxide (4·0 ml. of 15·0 N) and dissolved in oxygen-free water (15 ml.) saturated with hydrogen. Ammonium chloride (2·0 g.) was added, and when dissolved, followed dropwise with stirring by acetic acid (2·0 ml. of 17·4 N). This solution was at approximately 30° C. A further solution, as follows, was prepared and added rapidly with vigorous stirring to the first solution. Freshly prepared copper (I) chloride (3·72 g.; 0·0376 g. mole) was dissolved in oxygen-free water (20 ml., saturated with hydrogen) containing ammonium chloride (10 g.) and two drops of 10 N hydrochloric acid, by warming and shaking alternately in a stoppered flask. The temperature of this last solution never exceeded 50° C. After mixing, the reaction vessel was stoppered and shaken vigorously cooling under the tap till a felted mass of crystals appeared. If crystals fail to appear it is necessary to cool by shaking in ice water. The crystals were rapidly filtered and washed with absolute alcohol (200 ml.). They were then transferred to absolute alcohol (500 ml.) in a stoppered container and thoroughly dispersed with vigorous shaking. The crystals were again filtered and washed with absolute alcohol (200 ml.) followed by chloroform (100 ml.) and the last traces of chloroform removed in a vacuum phosphorus pentoxide desiccator under suction. This gave 2·0–2·5 g. (39–48% yield) of violet prisms. The compound lost 2·7% of its weight in a phosphorus pentoxide-sodium hydroxide desiccator under vacuum (water pump) over a period of four days, and the colour changed to mauve. The colour changed similarly on heating at 70–80° C. for 45 min. and the compound (NH_3, 16·4%) lost 3·0% of its weight, which could not be accounted for by loss of ammonia (NH_3, 16·1%). The compound is rapidly oxidized in moist air and the colour changes to greenish-blue. If the compound was not thoroughly washed with absolute alcohol the ammonia and chlorine contents were extremely high due to contamination with ammonium chloride.

Found: Cu (total), 44·8, 44·9; Cu^{++}, 15·7, 15·9, 16·5, 17·0; NH_3, 16·44, 16·42; Cl, 34·9%.

Calculated for $[Cu^{II}(NH_3)_4][Cu^{I}Cl_2]_2 . H_2O$: Cu (total), 45·53; Cu^{++}, 15·18; NH_3, 16·27; Cl, 33·86; H_2O, 4·30%.

Bis-ethylene Diamine Copper (II) Dichloro Cuprate (I) Copper (I) Chloride . (VI). Anhydrous copper (II) chloride (1·22 g.; 0·0091 g. mole) was dissolved in oxygen-free water (25 ml.) followed by ethylene diamine (1·61 ml. of 69%; 0·0182 g. mole) and potassium chloride (2·0 g.). The mixture was then heated in a water bath to 70–75° C. whilst passing a steady stream of hydrogen. Freshly prepared copper (I) chloride (2·69 g.; 0·0272 g. mole) was dissolved in oxygen-free water (25 ml. saturated with hydrogen) containing potassium chloride (12·0 g.) and two drops of 10 N hydrochloric acid by heating to boiling, and this solution added dropwise with stirring to the previous one. The resulting mixture was cooled in ice-water to 25° C. in an atmosphere of hydrogen. The crystals were washed with 90% alcohol (50 ml.), followed by ether (50 ml.). Excess ether and moisture were removed in a phosphorus pentoxide desiccator under suction.

This gave 3·3 g. (66% yield) of purple prisms which were homogenous under the microscope. The compound is readily oxidized in air, when it assumes a blue colour.

Found: Cu (total), 46·0; Cu^{++}, 11·3, 12·4, 13·1; Cl, 32·3, 32·4%.

Calculated for $[Cu^{II}(NH_2 . CH_2 . CH_2 . NH_2)_2][Cu^{I}Cl_2]_2 . Cu^{I}Cl$: Cu (total), 46·08; Cu^{++}, 11·52; Cl, 32·15%.

The dichloro compound $[Cu^{II}(NH_2 . CH_2 . CH_2 . NH_2)_2][Cu^{I}Cl_2]_2$ would require Cu (total), 42·13; Cu^{++}, 14·04; Cl, 31·32%.

SUMMARY.

The reaction of one mole of tetrammine and bis-ethylene diamine copper (II) halides with two moles of the corresponding copper (I) halide dissolved in a concentrated solution of alkali halide has been found to yield highly coloured crystalline tetrammine copper (II) dihalogen cuprates (I) $[Cu^{II}(A)_4][Cu^{I}X_2]_2$. The bis-ethylene diamine copper (II) dichloro cuprate (I) could not be prepared but a compound $[Cu^{II}(en)_2][Cu^{I}_3Cl_5]$ was obtained if the mole ratio of bis-ethylene diamine copper (II) chloride to copper (I) chloride was 1:2 or 1:3. It is suggested that the extra molecule of copper (I) chloride is involved in the crystal lattice of the compound and that the ion $[Cu^{I}_3Cl_5]^{--}$ has no existence, but rather the compound is more correctly represented as $[Cu^{II}(en)_2][Cu^{I}Cl_2]_2 . Cu^{I}Cl$. The reactions of these compounds have been studied. An attempt to prepare a similar series with pyridine was unsuccessful.

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MAGNETIC PROPERTIES OF SOME TUNGSTEN BRONZES.

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Tungsten "bronzes" are not, as the name implies, alloys, but non-stoicheiometric compounds with the general formula R_xWO_3 where R is an alkali metal and x lies between 0 and 1. The bronzes possess striking colours, ranging from yellow through reddish brown to blue, which are no doubt due in some way to the fact that they contain both W^{V} and W^{VI}. Hagg (1935) has correlated the composition with colour, unit cell dimension and density of the sodium bronzes ; as x becomes smaller, that is, as more and more sodium ions are missing from the lattice, the cell dimension decreases and the colour changes from yellow to blue. In their optical properties the bronzes resemble the metals (Hagg, 1935). Nothing appears to be known of their magnetic properties (Selwood, 1943). An investigation of these properties was therefore undertaken in the hope of throwing further light on the constitution of the bronzes.

Since W^{V} contains one unpaired electron and W^{VI} none, it seemed probable that a knowledge of the magnetic moment* of a bronze might enable the calculation of the proportion of W^{V} to W^{VI} which could then be checked against chemical analysis.

Preliminary measurements of susceptibilities at room temperatures showed that there was no agreement between the values of x calculated from magnetic data using the relationship $\mu=2\cdot83\sqrt{\psi MT}$ and those found from chemical analysis. The magnetic method of calculating x is of course based on the assumption that the magnetic susceptibility is temperature dependent and follows the simple Curie Law ($\psi=C/T$). Because of the disagreement between the two values of x an attempt was made to discover whether the susceptibilities of the bronzes followed the Curie-Weiss Law ($\psi=C/T+\triangle$) or whether they were not independent of temperature altogether. Over the range of temperature studied (290–480° K.) it was found that, within the limits of experimental error, susceptibilities were in fact temperature independent.

Experimental.

Several sodium and potassium tungsten bronzes were made by fusing tungstic acid and alkali carbonate in different proportions and reducing the powdered fusion product by heating at a red heat under a stream of coal gas for several hours (Phillipp, 1882). The resulting bronze was then treated successively with boiling water, potassium hydroxide solution, hydrochloric acid, aqua regia, potassium hydroxide solution and finally water. When examined under the microscope the preparations appeared to be homogeneous. The products were analysed by using the method of Schaefer (1904). Several sodium bronzes were also examined by X-ray powder diffraction methods. (Hagg, 1935) and except in one instance there was reasonable agreement between the values of x derived by the chemical and X-ray methods. In that one case the X-ray value of x was adopted.

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* Magnetic moment, μ of an atom (in Bohr magnetons) is related to the number of unpaired electrons (n) it contains by the formula $\mu=\sqrt{n(n+2)}$.

Magnetic measurements were made by means of the Gouy method using an analytical balance sensitive to 0·1 mgm. Tubes were calibrated with $CuSO_45H_2O$ assumed to have a susceptibility $5{\cdot}92\times10^{-6}$ at 19° C. (Mellor, 1943). The diamagnetic corrections used were those quoted by Van Vleck (1932). Measured susceptibilities were usually so small that they were of the same order as the diamagnetic corrections. No great accuracy can therefore be claimed for moments derived from these measurements.

RESULTS.

Some typical measurements at room temperature are shown in Table I.

TABLE I.

Specimen.	$\psi\times10^6$	M.W.	$\psi_M\times10^6$	Diamagnetic Correction.	$\psi_A\times10^6$	μ_{eff} Bohr Magnetons.
Sodium bronze—						
I	0·20	248·0	50	40·7	90	0·46
II	0·43	251·6	110	41·3	150	0·59
III	0·42	252·7	110	41·6	150	0·59
Potassium bronze—						
I	0·20	256·6	50	48·7	100	0·48
II	0·13	254·3	30	47·3	80	0·44
III	0·22	261·7	60	50·5	110	0·52

On the assumption that μ_{eff} for one unpaired electron spin is $1{\cdot}73\mu_B$* the above values were used to calculate the proportion of W^V in each specimen and thereby the value of x.

From Table II it is clear that " spin only " theory which accounts so satisfactorily for the moments of many transition elements is not applicable to the tungsten bronzes. The moments in these substances are much smaller than required by this theory.

TABLE II.

Specimen.	μ_{eff} (obs.)	x from Magnetic Data.	x from Chemical and X-ray Analysis.	Predicted Value of μ_{eff} Calculated from x.
Sodium bronze I	0·46	0·10	0·6–0·7	1·38
Sodium bronze II	0·59	0·16	0·92	1·64
Potassium bronze I ..	0·48	0·09	0·63	1·29
Potassium bronze II ..	0·44	0·09	0·57	1·21

Measurements on several bronzes were next made over a range of temperatures (292–485° K.). Specimens were heated in a small, tubular, non-inductively

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* This is the theoretical value. Few experimental values for the moment of W^V are available but those reported are lower (1·53). Adoption of this lower value would not affect the conclusion of the present paper.

wound electric furnace mounted between the pole pieces. Although the furnace was made as small as possible, the pole pieces had to be moved further apart than in the previous experiments. The consequent weakening of the field further reduced the accuracy of measurements. The results for two bronzes are summarized in Table III.

TABLE III.

The Magnetic Susceptibility of Some Tungsten Bronzes at Different Temperatures.

Specimen.	Temperature. (° K.)	Magnetic Susceptibility. ($\times 10^6$.)
Sodium bronze III ($Na_{0\cdot9}WO_3$) ..	292	$0\cdot45 \pm 0\cdot03$
	400	$0\cdot45 \pm 0\cdot04$
	419	$0\cdot43 \pm 0\cdot03$
	430	$0\cdot41 \pm 0\cdot03$
	443	$0\cdot42 \pm 0\cdot03$
	452	$0\cdot40 \pm 0\cdot04$
	456	$0\cdot41 \pm 0\cdot03$
	461	$0\cdot43 \pm 0\cdot03$
	469	$0\cdot40 \pm 0\cdot03$
	482	$0\cdot35 \pm 0\cdot07$
	485	$0\cdot33 \pm 0\cdot07$
Potassium bronze II ($K_{0\cdot6}WO_3$)..	300	$0\cdot15 \pm 0\cdot04$
	415	$0\cdot12 \pm 0\cdot04$
	432	$0\cdot10 \pm 0\cdot04$
	444	$0\cdot14 \pm 0\cdot04$
	455	$0\cdot14 \pm 0\cdot04$
	457	$0\cdot13 \pm 0\cdot04$

From Table III it is evident that over the limited temperature range studied susceptibility is independent of temperature within the limits of experimental error.

This temperature-independent paramagnetism is consistent with the view that the tungsten bronzes contain quasi-metallic electrons.* Pauli's (1927) explanation of the temperature independent paramagnetic susceptibility of metals is applicable here. All electrons not in closed shells are partly free to move in permitted energy zones in the solid and to pair with electrons from other atoms. As the temperature increases, the number of unpaired electrons is increased, many electrons having been raised to higher energy levels. The number of unpaired electrons at the lower temperatures is smaller than it would be if the electrons were firmly bound, thus accounting for the low value of the observed moments. However, the increase in temperature also results in an increasing tendency to random orientation of unpaired spins. The two effects approximately cancel each other, so that paramagnetic susceptibility due to partially free electrons is roughly temperature-independent.

SUMMARY.

Tungsten bronzes show a small paramagnetic susceptibility which is roughly temperature-independent—at least in the range 290–470° K. This susceptibility is due to partially free electrons and is consistent with the view that the tungsten bronzes are semi-conductors.

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* Tungsten bronzes show the marked increase in electric conductivity with increasing temperature which is characteristic of semiconductors. Thermo-electromotive force measurements show that the bronzes are electron conductors (private communication from Dr. J. S. Anderson, Chemistry Department, University of Melbourne).

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DISPROPORTIONATION EQUILIBRIA IN ALKALINE EARTH IONS.

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Introduction.

Experimental work on disproportionation equilibria in inorganic systems is very meagre. On the other hand, the study of these equilibria in organic systems is comparatively advanced, due in large part to the investigations of Michaelis and his co-workers. The advances in the organic field have all followed upon the discovery (made independently by Michaelis and Elema (1931)) that analysis of the potentiometric titration curves of many reversible organic redox systems involving the overall transfer of more than one electron shows the presence in solution of compounds of oxidation state intermediate between the oxidation states of oxidant and reductant, and in thermodynamic equilibrium with these species, i.e. of semiquinones. When this was established, the problem of assigning structures to compounds isolated from such mixtures, the empirical formulæ of which could not be reconciled with classical valence concepts, was largely solved: they were shown to be either monomeric or dimeric semiquinones.

The absence of similar advances in the inorganic field is due to the fact that there are very few inorganic redox systems involving disproportionation which can be studied in this comparatively straightforward way. The reason for this is also the reason why semiquinone radicals have not been detected until recently—viz. that the potentiometric method is relatively insensitive, and intermediate formation can be detected by means of it only when the disproportionation constant (equilibrium constant of the reaction 2 (Int.)$\rightleftarrows$(Ox.)+(Red.)) is less than 10^2. The disproportionation constants in simple inorganic systems are in general either much larger than 10^2 or so much smaller that one ion of limiting state exists only in minute amount in equilibrium with the intermediate and the other ion: hence ions to " anomalous " valence states commonly escape detection in multivalent redox reactions. Other methods must, in general, be employed to detect such ions. The discovery of the Sn^{3+} ion in aqueous solution in equilibrium with Sn^{2+} and Sn^{4+} was made by Ball, Wulfkuehler and Wingard (1935) by the use of magneto-optical techniques, and the discovery of Cd^+ and Zn^+ as intermediates in the reduction in aqueous solution of the divalent ions was made by Prytz and Østerud (1942) and Heyrovsky (1947) by the use of ingenious polarographic methods.

While it must be recognized that present knowledge of disproportionation equilibria in inorganic systems is fragmentary, the principles of such equilibria established by the study of organic redox systems provide a guide to investigation in this field. One fact in particular that is illustrated by the discovery of semiquinones and which is true for any system, organic or inorganic, must be emphasized: it is that whenever an ion, element or molecule of oxidation state x is in thermodynamic equilibrium with an ion in solution of oxidation state x+n, there exist also in solution ions of all oxidation states from x+(n−1) to x+1 where n is positive, or from x+(n+1) to x−1 where n is negative, in disproportionation equilibrium with these species. The validity of this is seen when it is realized that to deny it is, in the case of inorganic ionic systems, to assert that there is in some cases an infinite difference of free energy between aqueous ions of the same element but of different oxidation states.

This immediately rules out such confused notions as Kirk and Browne's (1928) concept (independently suggested by Shaffer (1933)) of "didelectronators", i.e. molecules or ions which can accept from reductants no less than two electrons. In spite of this, however, the possibility of some ions acting as pure "didelectronators" is still being investigated by Remick (1947). It is symptomatic of the unsatisfactory state of disproportionation theory that this error is repeated by Wilson and Bremner (1948) in the only comprehensive review of inorganic disproportionation equilibria yet published. These authors remark (*op. cit.*, p. 2): "If we consider the reaction when a biavlent metal is oxidized to a salt $M-2e=M^{2+}$, a bivalent oxidation, we can see that if the metal has only one state of valency, e.g. magnesium, the reaction cannot proceed in any other way—there are no univalent compounds of magnesium." (Presumably this is also considered to be true of all the alkaline earths, since no equilibria involving +1 ions of any metal of this group is discussed by these authors.) Apart from the general issues (the most important of which is the suggestion that the existence of ions of intermediate valence states in *compounds* of an element is a criterion of the existence of these ions in solution) a more unfortunate example could scarcely have been chosen: for of all the alkaline earth metals, magnesium is the one of which the greatest number of compounds containing the metal in oxidation state +1 is known, the most important of these being the Grignard reagents.

In this paper, the evidence for the existence of disproportionation equilibria involving alkaline earth ions of oxidation state +1 in the vapour, liquid and solid states, and in aqueous and non-aqueous solution, is discussed. It is shown that the lack of general recognition of the existence of these equilibria is inconsistent with experiment. The existence of these equilibria in a group of elements in which this might be thought to be unlikely (all the commoner compounds of the alkaline earths containing the ions of oxidation state +2) is a confirmation of the view that disproportionation equilibria are at least as widespread and of equal importance in the inorganic as in the organic field.

THE M/M$^+$ POTENTIALS IN AQUEOUS SOLUTION AND THE DISPROPORTIONATION EQUILIBRIUM.

The theoretical calculation of intermediate potentials has not hitherto been attempted. In a recent publication,* however, it was shown that the free energy of formation of an aqueous ion ($\triangle F_f^\circ$) may be calculated when the free energy of sublimation ($\triangle F_s^\circ$) and ionization ($\triangle F_i^\circ$) of the element, and the real free energy of hydration of the ion ($\triangle F_h^\circ$) are known, according to Eq. 1.

$$\triangle F_f^\circ = \triangle F_s^\circ + \triangle F_i^\circ + \triangle F_h^\circ - z\,(103\cdot92)\ \text{Kcal.} \quad \ldots\ldots\ldots\ldots (1)$$

In the same publication it was shown that the real free energy of hydration of cations of noble gas structure may be accurately calculated by means of the modified Born equation 2,

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* Hush (1948).

$$-\Delta F_h{}^\circ = \frac{Nz^2e^2}{2(r_c+0\cdot 86)}\,(1-1/D)+6\cdot 9z \text{ Kcal.} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where z is the valency and r_c the Pauling crystal radius of the ion.†

The application of Eq. (2) is in general restricted to ions of noble gas structure since it has been assumed, in deriving the equation, that the hydration energy is entirely electrostatic in nature ; this will be the case only when the polarizability of the ion is small in comparison with the crystal radius (as in ions of this kind), entailing that the van der Waals potential of the ion is small and of the same order as that of the substituted water molecules. Within the accuracy of these calculations, this may also be assumed true of univalent ions of the alkaline earth elements. The crystal radii of the univalent ions are of course not directly known, but they have been estimated from the radii of the divalent ions by means of the relationship $r_c(M^+)=r_c(M^{2+})+0\cdot 16$ Å. The real free energies of hydration of the univalent alkaline earth metals, on these assumptions, are as shown in Table 1.

TABLE I.

Real Free Energy of Hydration of Univalent Gaseous Alkaline Earth Ions.

Ion.	r_e (Å.)	$-\Delta F_h{}^\circ$ (Kcal.)
Be^+	1·33	129·3
Mg^+	1·67	104·4
Ca^+	2·01	87·9
Sr^+	2·15	82·6
Ba^+	2·37	76·6

With the values of $\Delta F_h{}^\circ$ thus calculated, the potentials M/M^+ may be evaluated according to Eq. (1). This calculation is shown in Table II. The potentials M^+/M^{2+}, which have been calculated from the relationship $E(M^+/M^{2+})=2E(M/M^{2+})-E(M/M^+)$, are also included.

TABLE II.

Normal Potentials M/M^+ and M^+/M^{2+} of the Alkaline Earth Metals.

Metal.	$-\Delta F_h{}^\circ$ (Kcal.)	$\Delta F_i{}^\circ$ (Kcal.)	$\Delta F_s{}^\circ$ (Kcal.)	$\Delta F_f{}^\circ$ (Kcal.)	$E_0(M/M^+)$ (v.)	$E_0(M/M^{2+})$ (v.)	$E_0(M^+/M^{2+})$ (v.)
Be ..	129·3	214·0	66·0	46·8	+2·1	—1·7	—5·5
Mg ..	104·4	175·6	27·6	—4·3	—0·2	—2·3	—4·4
Ca ..	87·9	140·5	34·5	—17·0	—0·7	—2·9	—5·1
Sr ..	82·6	130·8	30·7	—25·0	—1·1	—2·9	—4·7
Ba ..	76·6	119·8	41·4	—19·3	—0·8	—2·9	—5·0

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† An example will be given to illustrate the accuracy of this method. The ion Sr^{2+} has a noble gas structure, hence the potential Sr/Sr^{2+} may be calculated according to Eqs. (1) and (2), given the values of r_c, $\Delta F_s{}^\circ$ and $\Delta F_i{}^\circ$. The value of r_c is 1·13 A. ; thus according to Eq. 2, $\Delta F_h{}^\circ$ is —341·1 Kcal. Substituting in Eq. 1, using the known values of $\Delta F_i{}^\circ$ and $F_s{}^\circ$, we obtain $-\Delta F_f{}^\circ = -385\cdot 51-30\cdot 70+341\cdot 1+207\cdot 84=132\cdot 7$ Kcal. The calculated Sr/Sr^{2+} potential is thus —2·88 v. on the absolute hydrogen scale, as compared with the experimental value of —2·90 v. In general, an accuracy of the order of ±0·1 v. is to be expected in the theoretical calculation of potentials.

It is evident that the normal potentials for the two one-electron steps of the oxidation of alkaline earth metals to oxidation state +2 or reduction of the divalent ions to oxidation state 0 are in inverse order, and so widely separated that the disproportionation equilibrium in aqueous solution $2M^+ \rightleftarrows M + M^{2+}$ lies far to the right. The constant for this equilibrium in each of the systems may be calculated from the potential data of Table II, since the free energy of disproportionation ($\triangle F_d$) is given by

$$\triangle F_d^\circ = \triangle F_f^\circ(M^{2+}) - 2\triangle F_f^\circ(M^+)$$

The values of $\triangle F_d^\circ$ and the equilibrium constant in each case are shown in Table III.

TABLE III.

The Free Energy of Disproportionation of Aqueous M^+ Ions.

Metal.	$-\triangle F_d^\circ$ (Kcal.)	Log K_d.
Be	172	126
Mg	99	73
Ca	99	73
Sr	83	61
Ba	98	72

From the high values of K_d for each of these systems, it may be inferred that (monomeric) salts of +1 ions of the alkaline earths cannot be isolated from aqueous solution. In order to isolate such salts, it would be necessary that the ratio of the solubility product of the divalent compound to that of the monovalent compound, in the case of salts with a divalent anion (and that the ratio of the solubility product of the divalent compound to the square of that of the monovalent compound, in the case of salts with a monovalent anion) be 10^{126} for Be salts and of the order of 10^{70} for the remaining alkaline earth salts. It is evident, however, that this is highly unlikely; it can be calculated that in the case of halides, assuming* the lattice energies of the +1 salts to be approximately those of the corresponding alkali halides, the ratio does not differ significantly from 1.†

The high value of K_d for these systems would also be expected to affect the kinetics of reactions in which aqueous +2 ions are reduced to the metal, or the metal is oxidized to aqueous +2 ions. The only published data which is relevant to this appears to be that on the rate of solution of the alkaline earth metals in water and acids, and although these reactions are too complex to be discussed in any detail here, it may not be coincidental that those metals of the alkaline earth group which are not oxidized by hydrogen ion in pure water at room temperature (viz. Be and Mg) even though the M/M^{2+} potentials are in each case sufficiently low to make this thermodynamically possible, are also the metals for which the potential of the first step of reduction is higher than that of the hydrogen/hydrogen ion couple at pH 7 (−0·41 v.). ‡

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* The approximate correctness of this assumption is shown in the next section.

† This calculation makes use of the hydration energies derived above for the monovalent ions and those already published (Hush, *op. cit.*) for the divalent ions and the halide ions.

‡ The connection between high value of dismutation constant and sluggishness of reaction has been discussed by Michaelis (1937).

No account has been paid so far to the possibility of dimerization of the aqueous M^+ ions by pairing of the 3s electrons, although this probably occurs. Such dimerization, if it occurs, will of course not affect the above derivation of intermediate potentials, but will nevertheless result in increased stability of the +1 form. No calculations of the dimerization equilibria can be made, but even if dimerization is practically complete it cannot be expected that solid salts containing dimerized M^+ ions will be isolated from aqueous solution. Such salts would only be isolated if the values of $\triangle F$ for the reaction $2M^+ \rightarrow (M^+)_2$ were of the order of -100 to -170 Kcal., and this is most unlikely.

ALKALINE EARTH SUBHALIDES IN THE VAPOUR AND CRYSTALLINE STATES: HEATS OF FORMATION, DISPROPORTIONATION AND DIMERIZATION.

The existence of alkaline earth subhalides, in which the metal is in oxidation state +1, has been debated, but in fact sufficient data are available to make possible the deciding of this issue.

There is no doubt that halides of formula MX exist in the vapour state at *ca.* 1000° C. in equilibrium with the metal and the divalent compounds. The absorption spectra of alkaline earth halides in the visible and ultra-violet were examined by Walters and Barratt (1928), and bands were identified as being due to the presence of each halide (F, Cl, Br and I) of Mg, Sr, Ca and Ba. These were shown to be not dimers of formula M_2X_2, but monomers of formula MX. Johnson (1929) examined the band spectra of MgF, CaF and BaF in the vapour state and deduced the energy of dissociation of CaF into gaseous atoms. Parker (1935) published a vibrational analysis of band systems due to MgCl, CaCl and SrCl vapour.*

Crystalline products of reaction between normal alkaline earth halides and the metal at high temperature, of empirical formula MX, have long been known. A crystalline product of empirical formula CaCl was obtained during electrolysis of fused $CaCl_2$ by Borchers and Stockem (1902, 1903) and Danneel and Stockem (1905). This product was obtained by Wöhler and Rodewald (1909) by heating metallic Ca with $CaCl_2$ in equivalent proportions at 900–1000° C. in a steel cylinder, and by Benoit and Guntz (1924) in a similar fashion. Crystalline products of empirical formulæ CaF and CaI were obtained by Wöhler and Rodewald (1909) by the same method as used in the preparation of CaCl, the temperatures being 1400° C. and 800° C. respectively. A double salt NaF.BaF was obtained by Guntz (1902), by heating NaF with BaF_2 at 800° C. An almost theoretical yield of a crystalline product of empirical formula BaCl was obtained by Haber and Tolloczko (1904) and by Haber (1908) by the electrolysis of fused $BaCl_2$ in a nitrogen atmosphere at 600° C. The same product was obtained by Benoit and Guntz (1924) by heating metallic barium with $BaCl_2$ at high temperature. These authors also prepared BaBr, BaF and BaI. A double compound of BaF with NaF was described by Guntz (1902). Benoit and Guntz also obtained SrCl, SrBr, SrF and SrI by their usual method.

The facts which appear to be decisive in favour of the view that these compounds are actually subhalides, and not mixtures or solid solutions of the metal and the dichloride are the following:

(i) The salts retain their characteristic properties after precautions have been taken to remove excess metal and dichloride. Thus Wöhler and Rodewald purified their compounds by suspending the salts first in ethyl iodide, thus precipitating any excess metal, and then in bromoform, thus separating excess dichloride.

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* The spectrum of MgF has also been investigated by Jenkins and Grinfeld (1933, 1934) and (together with that of BeF) by Jevons (1929).

(ii) The colours, streaks and lustres of the salts are those characteristic of compounds of unstable valence type, and could not be accounted for on the mixture or solid solution hypotheses. Calcium subchloride, according to both Wöhler and Rodewald (1909) and Borchers and Stockem (1902) form bright red to violet pleochroic crystals. Calcium subfluoride and calcium subiodide form (according to Wöhler and Rodewald) respectively red-orange and brown crystals, the subfluoride having a metallic lustre. The strontium and barium subhalides, according to Benoit and Guntz (1924) are all deep brown, the barium salts having a violet streak.

(iii) The heat of interaction of the metal and the metal chloride to form MX may be calculated from the data of Benoit and Guntz on the heat of solution of the subchlorides in acid. These are (at least in the case of Ba and Sr) of the order of $-\triangle H=16$ Kcal. for the reactions of $M+MX_2 \rightarrow 2MX$, which are larger than could be expected for the formation of a solid solution.

Taking it that the salts are subhalides, containing the metal in oxidation state +1, the question may now be asked whether these salts are simple monomers of formula MX, or dimers, or perhaps higher polymers. This may be approached in the following manner. Since the heats of formulation of gaseous M^+ and X^- are known, the heat of formation of $MX(_c)$ could be calculated by means of a Born-Haber cycle if the lattice energy of MX were known. If the salt is a monomer, one may assume the lattice energy to be that of the corresponding alkali halide, with tolerable accuracy and thus the heat of formation may be approximated: this will actually lead to a slightly high value of $-\triangle H_f{}^\circ(_c)$, since the alkaline earth ions have larger radii. For the sub-fluorides, these values may be checked by an independent calculation, employing the data of Johnson (1929) for the heats of dissociation into gaseous atoms, assuming that the heats of sublimation of the subfluorides are approximately the same as those of the corresponding alkali fluorides. From the heat of formation, one may calculate the heat of the disproportionation reaction $MX \rightarrow \frac{1}{2}M+\frac{1}{2}MX_2$. These calculations for Mg, Sr and Ca are shown in Table IV.

The approximate agreement of the values of $\triangle H_f{}^\circ(c)$ calculated independently for CaF and SrF by methods (*a*) and (*b*) is good evidence that these figures are of the correct order of magnitude—i.e. that the reaction $M(c)+\frac{1}{2}X_2(g) \rightarrow MX(c)$ is exothermic to the extent of about 60 Kcal. It may be assumed that the entropy changes in these reactions are small,* so that the heats and free energies of reaction may be assumed to be of approximately the same order of magnitude. It is then seen that, in spite of the large negative value of $\triangle H_f{}^\circ(c)$, the heat of disproportionation is so large that subfluorides of these alkaline earth metals of formula MX are so unstable with respect to the decomposition $MX(c) \rightarrow \frac{1}{2}M(c)+\frac{1}{2}MX_2(c)$ that it is impossible that a crystalline monomeric subfluoride could be isolated. Calculations of $\triangle H_d{}^\circ$ for other subhalides of alkaline earth metals by the same method as employed in Table IV have been made by Grimm and Herzfeld (1923); the values are in every case of the same order of magnitude as those of the subfluorides, and it is thus possible to generalize, and to assert that *no crystalline alkaline earth subhalide has the simple monomeric formula MX.*

The most probable alternative is that the subhalides contain $(M\text{-}M)^{2+}$ ions, formed by pairing of the lone 3s electrons (cf. mercurous halides), and are thus dimeric, represented by the formula $(M^+)_2X_2$. The energy relationships on this view may be worked out from the data of Benoit and Guntz (1924) on the heats of solution of the subchlorides of Ba, Sr and Ca in dilute acid. The net process

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* Cf. Latimer (1938).

TABLE IV.

Approximate Theoretical Heats of Formation and Disproportionation of Monomeric Alkaline Earth Subfluorides.

Salt.	$\triangle H_f^\circ(g)$ (Kcal.)	$\triangle H_s^\circ$ (Kcal.)	$\triangle H_f^\circ(c)$ (Kcal.)		$\triangle H_d^\circ$ (Kcal.)
			(a)	(b)	
MgF ..	—	72	—	—68	—64
CaF ..	3	50	—47	—69	—76
SrF ..	2	53	—51	—71	—74

$\triangle H_f^\circ(g)$: heat of the reaction $M(c)+\frac{1}{2}X_2(g)\rightarrow MX(g)$, from data of Johnson.*

$\triangle H_s^\circ$: heat of sublimation of MX(c), assumed to be equal to the heat of sublimation of the corresponding alkali fluoride.

$\triangle H_f(c)$: heat of the reaction $M(c)+\frac{1}{2}X_2(g)\rightarrow MX(c)$; (*a*) calculated from $H\triangle_f^\circ(g)$ and $\triangle H_s^\circ$, (*b*) calculated by means of a Born-Haber cycle, assuming the lattice energies of the subfluorides to be those of the corresponding alkali fluorides.

$\triangle H_d^\circ$: heat of the disproportionation reaction $MX(c)\rightarrow\frac{1}{2}M(c)+\frac{1}{2}MX_2(c)$ calculated from $\triangle H_f^\circ(c)$ derived by method (b) and the heat of formation of $MX_2(c)$.

* There appears to be some confusion in the derivation of $\triangle H_f^\circ(g)$ values for SrF and MgF by Bichowsky and Rossini (1936) which has misled later investigators (e.g. Latimer, 1938). In the text, Bichowsky and Rossini state that Johnson (1929) gave values for the energy of dissociation (D) of MgF, CaF and SrF into gaseous atoms. In the table, the only value of D shown is for SrF, given as 77 Kcal. The heats of formation of MgF, CaF and SrF are given in the table as 95, 3 and 27 Kcal. In the reference cited, however, Johnson reports only one value of D, viz. that of CaF ; this is given as 77·46 Kcal. (assuming the Ca atom to be in the 2^3P state). It is remarked that the dissociation energy of SrF is probably of the same order as this, and in the calculation of $\triangle H_f^\circ(g)$ in Table IV it has been assumed to be the same. The value of D for MgF is not discussed by Johnson. The value of D for CaF cited gives (together with the heats of sublimation of Ca(c) and dissociation of $F_2(g)$) $\triangle H=3$ for the reaction $Ca(c)+\frac{1}{2}F_2(g)\rightarrow CaF(g)$. Assuming as a first approximation that D for SrF is also 77 Kcal., we calculate for $Sr(c)+\frac{1}{2}F_2(g)\rightarrow SrF(g)$ $\triangle H=2$ Kcal. This latter value is in marked disagreement with that given by Bichowsky and Rossini. Since D for MgF has not been estimated, the heat of formation of gaseous MgF cannot be calculated in this manner.

of solution is represented by Eq. (iii) below ; this may be regarded as the sum of the two reactions (i) and (ii) :

$$(M^+)_2X_2(c) \longrightarrow M+M^{2+}(aq.)+2X^-(aq.) \quad \ldots\ldots\ldots\ldots \quad (i)$$

$$M+2H^+(aq.) \longrightarrow M^{2+}(aq.)+H_2(g) \quad \ldots\ldots\ldots\ldots \quad (ii)$$

$$(M^+)_2X_2(c)+2H^+(aq.)\rightarrow 2M^{2+}(aq.)+H_2(g)+2X^-(aq.) \quad \ldots\ldots \quad (iii)$$

Since the heats of reactions (ii) and (iii) are known, that of (i) may be calculated, and from this the heat of formation and disproportionation of $(M^+)_2X_2(c)$ evaluated in the usual way. The heat of dimerization may be evaluated with fair accuracy by estimating the heat of formation of the monomer MX(c) by the same method as employed in calculating $\triangle H_f^\circ(c)$ for the subfluorides in Table IV (in which a monomeric structure was assumed) and combining this with the actual heat of formation of the dimer. The values so obtained are shown in Table V.

From the data of Table V, it is evident that each subhalide, viewed as the dimer $(M^+)_2X_2$, has a large negative heat of formation, and that all are stable (although $(Ca^+)_2Cl_2$ is less so than the other two salts) to disproportionation. This is sufficient to account for the existence of the subhalides as fairly stable salts at ordinary temperature. This entails that the lattice energies of the subhalides approach the order of magnitude of those of the normal dihalides. The actual energies cannot be calculated exactly, since the heats of the reactions $2M^+(g)\rightarrow(M^+)_2(g)$ are not known. Assuming that these have approximately the same value in each case, and that this is of the order of magnitude of the heat of dimerization of gaseous alkali metal atoms, we may set $\triangle H$ for the above reaction very roughly at —10 Kcal. On this assumption, the lattice energies of $(Ba^+)_2Cl_2$, $(Sr^+)_2Cl_2$ and $(Ca^+)_2Cl_2$ respectively (calculated from a Born-Haber cycle) are 430, 460 and 460 Kcal. Comparison with the lattice energies of the corresponding dichlorides (474, 501 and 532 Kcal.) shows that, as would be expected, the lattice energies of the subchlorides are smaller than but of the same order as those of the dichlorides.

TABLE V.

Heats of Reaction of Subchlorides of Ba, Sr and Ca.

Metal	$\triangle H_f°(c)$ Calculated for Monomer. (Kcal.)	$\triangle H_f°(c)$ Calculated for Dimer. (Kcal.)	$\triangle H_D°$ Calculated for Dimer and Monomer. (Kcal.)	$\triangle H_d°$ Calculated for Dimer. (Kcal.)
Ba	—55·9	—222·4	—110·6	17·0
Sr	—42·2	—213·2	—128·8	15·2
Ca	—35·7	—194·0	—122·6	3·4

$\triangle H_f°(c)$, calculated for monomer: Heat of the reaction $M_c+\frac{1}{2}X_2(g)\rightarrow MX(c)$ calculated theoretically by means of a Born-Haber cycle, assuming the lattice energies of the monomeric subchlorides to be the same as those of the corresponding alkali chlorides.

$\triangle H_f°(c)$, calculated for dimer: Heat of the reaction $2M(c)+X_2(g)\rightarrow(M^+)_2X_2(c)$ calculated from the data of Benoit and Guntz (1924) on heats of solution, and heat of formation of M^{2+} (aq.).

$\triangle H_D°$: Heat of dimerization of MX(c), i.e. heat of the reaction $2MX(c)\rightarrow(M^+)_2X_2(c)$, calculated from $\triangle H_f°(c)$ values for monomer and dimer.

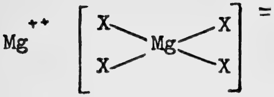
$\triangle H_d°$: Heat of the disproportionation reaction $(M^+)_2X_2(c)\rightarrow M(c)+MX_2(c)$ calculated from $\triangle H_f°(c)$ and heat of formation of $MX_2(c)$.

One important result of the positive values of heats of disproportionation of the solid subchlorides shown in Table V is the difficulty of electrolytic reduction of the dichlorides to the metal. This is so marked that, as has been pointed out above, electrolysis of the dichlorides has served as a preparative method for obtaining the solid subchlorides. Benoit and Guntz (*op. cit.*) found that barium could not be obtained by the electrolysis of barium chloride under any conditions, and that only a minute amount of strontium was obtained by electrolysis of strontium chloride, although in both cases the subchlorides were formed. A higher yield of the subchloride of barium from electrolysis was claimed by Haber and Tolloczko (*op. cit.*) who calculated from their potential data a value of 34·6 Kcal. for $\triangle H_d$ at 600° C., which is of the same sign as the value found for the reaction at 25° C. in Table V, and of an order of magnitude in reasonable agreement with it, the temperature effect being taken into account.

ORGANOMAGNESIUM HALIDES.

The formation of compounds of empirical formula RMgX (Grignard reagents), where R is an alkyl or aryl radical and X a halogen, by reacting metallic magnesium with the organic halide is well known. The reaction usually goes to completion in dry ether; it may also be carried out in toluene, benzene, xylene, petroleum ether and tertiary amines (Tschelinzeff, 1904) or in the complete absence of solvent (Lohr, 1891; Shoruigin and Isagulyantz, 1936). From each solvent, products RMgX may be isolated as crystalline solids, either solvent-free or, when the solvent molecule contains available co-ordination pairs, solvated.

There has been much controversy over the structure of Grignard reagents, and the problem has not been systematically investigated. The simple structure RMgX (I), in disproportionation equilibrium with R_2Mg and MgX_2 was proposed by Schlenk and Schlenk in 1929. The main alternative formulæ that have been discussed are those of Terentiev (1926), who proposed the ionic complex II, and Jolibois, who proposed the " loose complex " III for the non-solvated species.



II

III

The issues here are :

(i) Does a solution or a crystalline precipitate of a Grignard reagent contain a species $(RMgX)_n$ (i.e. either I, II or III) in equilibrium with the species MgX_2 and MgR_2?

(ii) If there is such an equilibrium, is the Mg in the first species in oxidation state +1?

(iii) If there is a species $(RMgX)_n$, is n equal to 1 or 2?

Discussion of these issues will be confined to the properties of Grignard reagents in solution, since little is known about the properties of the solid compounds. The first point may be answered definitely. Schlenk and Schlenk (1926) were able to isolate quantitatively $(RMgX)_n$ and MgX_2 from solutions of Grignard reagents by dioxane precipitation, leaving in solution R_2Mg, and by this method the position of equilibrium in many Grignard solutions was determined. A phenomenon which Schlenk and Schlenk were unable to explain—vix. that all Grignard solutions on continued standing slowly deposit MgX_2—was investigated more recently by Noller and Raney (1940). These authors propose new values for the equilibrium constants, but confirm the existence of the equilibrium in solution. The effect of various solvents on the equilibrium has been studied by Miller and Bachmann (1935). It may thus be assumed that the equilibrium exists.

The second point cannot be answered so definitely, since it is not easy to see what could conclusively distinguish a species of oxidation state +1 from the other alternatives, but all the evidence is consistent with the view that the magnesium is in this state. A large number of electrolysis studies have been made of Grignard reagents in ether solution, but the only point of interest is that the liberation of one equivalent of magnesium from a Grignard reagent requires one Faraday (Evans and Lee, 1934). Again, the rapid absorption of oxygen by Grignard reagents in ether solution, and their ready cleavage by halogens are properties that would be expected of intermediate compounds.

The third point is closely connected with the second. If the species in equilibrium with MgX_2 and MgR_2 is in fact RMgX, in which the Mg is in oxidation state +1, no dimerization can be expected, for the 3s electron of the metal ion which is responsible for dimer formation in the simple subhalides of the alkaline earth metals is already paired in the monomer RMgX. In agreement with this, both Schlenk and Schlenk (1926) and Noller and Raney (1940) found that the position of equilibrium in Grignard solutions is independent of total concentration, which indicates that the species in equilibrium with MgX_2 and MgR_2 is monomeric. It might be thought that confirming evidence for this could be obtained by molecular weight determination, but the work that has been done in this regard indicates that interpretation of boiling-point data is difficult.* There is, however, no good evidence against the view that at normal concentrations the species in equilibrium with MgX_2 and MgR_2 is the monomer RMgX.

The position is, then, that all available evidence is consistent with the Schlenk and Schlenk hypothesis. On the basis of this hypothesis, which is now generally accepted, even by those who formerly preferred an alternative view (e.g. Noller, 1940) reaction mechanisms can in general be explained, notwithstanding difficulties which are inevitable on any view. This hypothesis will therefore be assumed to be correct, and the following description will be taken to characterize the formation of a Grignard reagent :

A Grignard reagent is formed by the reaction of magnesium metal with an alkyl or an aryl halide, in the course of which the magnesium is oxidized by the halogen from oxidation state 0 to +1, the intermediate state being stabilized by pairing of the 3s electron of the Mg^+ ion with the free electron of the R radical, forming an organomagnesium subhalide of formula RMgX. The subhalide is in disproportionation equilibrium with the species R_2Mg and MgX_2.

There is further evidence for the existence of magnesium ions of oxidation state +1 in ether solution. Evidence for the existence of the equilibrium

$$MgI_2 + Mg \rightleftarrows 2MgI$$

in ether-benzene solutions of magnesium iodide in contact with metallic magnesium was put forward by Gomberg and Bachmann (1927) and Gomberg, Bailan and Van Natta (1929). It was shown that ether-benzene solutions of this type reduce aromatic ketones to the corresponding pinacols, often in quantitative yield, a reaction that is not effected by either Mg or MgI_2 alone. This is ascribed to the formation of a halomagnesium ketyl R_2COMgX by combination of the ketone with the intermediate MgK, followed by dimerization to give a halomagnesium pinacolate, $XMgC(R_2)C(R_2)MgX$. The deep colour (usually red) of the reaction mixture is probably due to the colour of the ketyl ; this is supported by the facts that the colour is easily destroyed by a trace of oxygen, and that the solutions do not obey Beer's law. The analogy between this reaction and the formation of sodium ketyls has been pointed out by Gomberg and Bachmann.

It has been suggested that the formation of carbinols by interaction of Grignard reagents with ketones has a free radical mechanism, involving the intermediary formation of halomagnesium ketyls of the type discovered by Gomberg and Bachmann (Blicke and Powers, 1929). This cannot be the case, for in reactions of this sort no appreciable quantities of R-R compounds of any sort are formed. In this connection it is interesting to note that under conditions in which the $2Mg^+ \rightleftarrows Mg + Mg^{2+}$ equilibrium would be expected to shift far to the right, without any net oxidation or reduction taking place, a Grignard reagent splits up, yielding R-R compounds, indicating the liberation of free radicals in the process. Thus it was shown by Colburn (1940) that addition of a catalytic quantity of water to an ether solution of phenylmagnesiumbromide resulted in the formation of large amounts of diphenyl. This appears to be a general reaction.

Finally, it may be observed that although some perplexities have arisen in Grignard chemistry owing to the fact that in many cases the treatment of carbonyl compounds with MgR_2 or with a Grignard reagent RMgX yields substances which give identical hydrolysis products (e.g. the discovery of Noller, 1931, that ether solutions of di-isobutyl magnesium which are practically halogen-

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* Terentiev (1926) has published data which do not appear to be in accordance with this, but the methods employed by this author have been criticized by Meisenheimer and Slichenmaier (1928).

free reduce benzophenone to benzohydrol as well as the original Grignard reagents) reactions of this sort are not to be taken as evidence against the existence of RMgX, in which the magnesium is in the intermediate oxidation state, in Grignard solutions. The action of water on both RMgX and R_2Mg results in (i) oxidation of the magnesium (from oxidation state 0 or +1) to oxidation state +2; (ii) reduction of the organic radical R. Difference in the nature of the final products will be expected only when the initial reaction with the carbonyl compound modifies the R groups of either the carbonyl compound or the Grignard reagent. In general this modification will be expected in the action of the Grignard reagent, rather than R_2Mg, on the carbonyl compound, owing to the large I_S effect of the magnesium ion. Thus according to Bartlett and Berry (1934) cyclohexene oxide reacts with Et_2Mg and Me_2Mg without rearrangement to give, on treatment with water, respectively *trans*-2-ethyl and *trans*-2-methyl cyclohexanol. With the corresponding Grignard reagents, cyclohexene oxide yields ethyl- and methyl-cyclopentylcarbinol. Even if this order is sometimes reversed—i.e. if rearrangement occurs in the dialkyl magnesium reaction rather than the Grignard reaction—the difference of mechanism has still to be understood as a difference in type of reaction between a carbonyl compound on the one hand and an organomagnesium compound in which the magnesium is in oxidation state either 0 or +1 on the other.

SUMMARY.

The evidence for the existence of disproportionation equilibria involving +1 ions of the alkaline earth metals is reviewed. It is concluded that these equilibria exist in aqueous and non-aqueous solution, and in the solid and vapour states. Wherever possible, thermodynamic quantities are calculated. The role of these equilibria in reactions involving the alkaline earths is pointed out, and important points of connection between the study of disproportionation equilibria in the organic and the inorganic fields are indicated.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD, N.S.W.

PART IV. GEOLOGY OF THE GUNNEDAH-CURLEWIS DISTRICT.

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With Plate XVI.

(Presented by permission of the Under-Secretary for Mines.)

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INTRODUCTION.

The Gunnedah-Curlewis district is by far the most important section of the North-Western Coalfield from an economic point of view. Apart from Werris Creek, it is the only section in which coal mining has developed beyond the prospecting stage and which contains any appreciable reserves. A considerable amount of field-work has been concentrated in this section and most of the area shown on Plate XVI has been surveyed in close detail by means of a telescopic alidade and plane table.

Field-work commenced in 1945, continued throughout almost the entire field season in 1946 and part of 1947, and was completed this year. Several departmental reports have been made by the writer during the course of the present survey, and these contain information concerning coal production, the quality of the coal seams, prospecting, and history of mining operations. In these reports the correlation of the geological sequence with the type area in the Hunter Valley was based on the Werrie Basalts being of Upper Marine age. However, the geological survey of the Willow Tree district (Hanlon, 1947*a*, 1947*b*) showed that the Werrie Basalts form part of the Lower Marine Series, and this has necessitated a reclassification of much of the sequence.

Reports made prior to the present survey were by David (1886), Stonier (1890*a*, 1890*b*, 1893), Pittman (1897), Carne (1908), Harper (1911, 1925) and Kenny (1927, 1928). Professor L. A. Cotton made three private reports to the Gunnedah Colliery Co., which have been kindly made available to the writer.

TOPOGRAPHY AND ACCESS.

Gunnedah and Curlewis are both situated on the North-Western Railway line, being 295 and 285 miles respectively from Sydney. Access by road is good and main roads connecting with Tamworth, Narrabri, Coonabarabran and Quirindi are trafficable in all weathers. Some secondary roads, which cross black soil plains, become impassable after heavy rains.

The Namoi River and its tributary, the Mooki River, flow through mature valleys. Large areas of gently sloping alluvium occur along both rivers at a general level about 900 feet above sea level. Gunnedah, the main town in the district, is 876 feet A.S.L. and Curlewis 897 feet A.S.L. The river flat widens considerably to the north of Curlewis and extends westwards over the Booloocooroo Plain.

Most of the high points in the district are capped by dolerite. However, many of these cappings were probably intruded in the form of sills and occupy their present positions due to subsequent erosion of the overlying sediments It is considered that the present high ground formed areas of relative relief in Tertiary time when the dolerites were intruded. This point is elaborated later when considering the Tertiary igneous rocks.

The highest point in the district is King Jack Trigonometrical Station on Black Jack Mountain and is approximately 2,470 feet A.S.L. or 1,600 feet higher than Gunnedah township. A considerable part of Black Jack Mountain is over 2,000 feet A.S.L. and many hills rise to the 1,600 feet level.

Within the hills the creeks occupy narrow steep gullies, but, on reaching the plain level, many of them lose their identity and do not possess any defined channels extending to the Namoi or Mooki Rivers.

GEOLOGY.

The geological formations comprise the following:

- Tertiary to Recent alluvium.
- Tertiary Igneous Rocks.
- Triassic.
- Permian
  - Upper Coal Measures—Black Jack Formation.
  - Upper Marine Series (?)—Gladstone Formation.
  - Upper Marine Series—Porcupine Formation.
  - Lower Coal Measures(?).
  - Lower Marine Series.

It was originally considered that a group of acid lavas and tuffs which outcrop in and around Gunnedah were of Carboniferous age, but later work has shown that these rocks are interbedded with the Werrie Basalts and should be regarded as being of Lower Marine age. The nearest outcrops of Carboniferous rocks to the Gunnedah district occur in the Carroll area (Lloyd, 1933), east of the more westerly of the Mooki Thrusts. The formations listed above will now be described in order, commencing with the oldest.

Permian.

Lower Marine Series. The Lower Marine Series at Gunnedah comprises a group of lavas and tuffs of acid to intermediate composition, interbedded with amygdaloidal basalts, and discontinuous lenticular beds of sediments which are probably of fresh water origin. No marine fossils were found anywhere in this series in the Gunnedah-Curlewis district. The flows are considered to be the equivalents of the Boggabri Volcanics. (See Part VI of this series of papers.)

The lavas and tuffs are mainly rhyolites or felsites, but trachytes and andesites also occur. Although they form solid outcrops, micro-sections show them to be very much altered. The rhyolites tend to be porphyritic and many of them show well-developed flow structure. In some cases relics of spherulitic structure are present. The phenocrysts are badly altered and in some instances are entirely replaced by chalcedony and opaline silica. Micro-sections of the trachytes and andesites show them to be similarly altered. The flows are lenticular and the proportion of the total thickness of the Lower Marine section which they form varies markedly from place to place.

The amygdaloidal basalts are interbedded with the lavas and tuffs described above. They are all more or less decomposed and micro-sections reveal that they consist chiefly of felspar laths and contain relatively little ferro-magnesian minerals. The amygdules comprise mainly natrolite, calcite and chalcedony. It is considered that they are to be correlated with the Werrie Basalts, and the age of the whole group of lavas, tuffs, amygdaloidal basalts and sediments is therefore fixed as being Lower Marine (Hanlon, 1947*a*, 1947*b*). The maximum thickness of Werrie Basalts exposed in the Gunnedah district is 450 feet, along and to the west of the railway line south-west of Gunnedah township; The total thickness may be considerably greater, because it appears likely that the black soil plains to the east would be underlain by them, at least in part. The thickness of the Werrie Basalts varies considerably and immediately south and south-west of Gunnedah the section exposed along the railway line appears to have lensed out completely, Greta (?) sediments resting directly on Lower Marine sediments, which in turn overlie the rhyolites that outcrop in the town itself. Adjacent to the Mullaley Road, Upper Marine sediments rest directly on Lower Marine rhyolites.

The sediments comprise sandstones and conglomerates which are generally unfossiliferous. The only fossils found were fragments of *Glossopteris* in an isolated outcrop in portion 364, Parish of Gunnedah, County of Pottinger. The thickness of the sediments and their distribution is very irregular. An explanation would be that the Lower Marine lavas suffered contemporaneous erosion, the Werrie Basalts being removed in preference to the more resistant acid lavas, and irregular beds of sediments were deposited in the drainage channels and depressions so formed. The irregular thickness of the Werrie Basalts would thus be explained as being due partly to their having flowed over lower ground around the thickest acid lava flows and partly to having been eroded themselves and the drainage channels so formed filled with sediments. Alternatively, the Werrie Basalts may have been partly intrusive, an origin suggested for spilites in the Silverwood district and other parts of the world (Bryan, 1925).

Lower Coal Measures (?). There is a restricted outcrop to the south of Gunnedah, of shales containing abundant impressions of *Glossopteris*. There is no evidence of any coal seams being developed. The shales outcrop best in portions 202 and 209, Parish of Gunnedah. In portion 209 they appear to overlie directly the Lower Marine sediments, referred to above, in the region of their maximum development. In portion 202 they are underlain by basalt, which outcrops in the bed of a creek and is very much decomposed. It is probable that the outcrop forms part of the Werrie Basalts.

The shales are lenticular and their development dies out easterly, where the Werrie Basalts are overlain directly by definite Upper Marine sediments and westerly where the Upper Marine is resting on Lower Marine rhyolites. The shales have been classified as Lower Coal Measures because they contain *Glossopteris* and lie between Lower Marine beds and definite Upper Marine sediments. They could, however, represent the final phase in the development of the fresh water sediments which occur in the Lower Marine Sequence or a local development of fresh water sediments during Upper Marine time, prior to the onset of marine sedimentation throughout the area.

Upper Marine Series. It is proposed to name the definite Upper Marine beds the Porcupine Formation. It consists mainly of sandstones with beds of conglomerate. Bands of limestone occur near the top of the sequence, but shales are present only to a minor extent. The occurrence of an erratic containing *Spirifer disjuncta* Sowerby proves that there was contemporaneous ice action, which also probably contributed to the poor sorting of the sediments in some places. There are two main areas of development, one immediately west and south of Gunnedah, especially in the Porcupine Hill area adjacent to the North-Western Railway line, where they form a prominent escarpment 400–500 feet above rail level, and the other to the east and south-east of Curlewis. They form a belt to the north-east of the Upper Coal Measures and probably underlie the alluvium of portion of the Booloocooroo Plains.

Kenny (1928) classified the beds near Gunnedah with the Upper Coal Measures, although he suggested (unpublished report) that they may form part of the Upper Marine Series. The fossils discovered during the course of the present survey place the marine origin of the beds beyond doubt. The most comprehensive suite of fossils was obtained from portions 195 and 196, Parish of Curlewis, County of Pottinger, and contained the following:

Crinoid stems.
Fenestrellina spp.
Protoretepora ampla Lonsdale.
Stenopora tasmaniensis Lonsdale.
Astartila danai de Koninck.
Strophalosia gerardi King.
Strophalosia jukesi Etheridge.
Spirifer duodecimcostata McCoy.
Aviculopecten sprenti Johnston.
Deltopecten subquinquelineatus McCoy.
Terrakea brachythœra (Sowerby).
Terrakea fragile (Dana).
Dielasma inversa de Koninck.
Conocardium australe (Morris).
Ptychomphalina morrisiana McCoy.
? Pleurotomaria morrisiana McCoy.
? Platyschisma sp. nov.

Mr. H. O. Fletcher (private communication) states: "In the above Permian fauna there is an abundance of the genus *Strophalosia* and *Terrakea.* This association is somewhat characteristic of the fossil fauna found in the Muree Stage of the Upper Marine Series and in equivalent beds of the Illawarra district. In all probability the marine beds at Curlewis are of a similar age."

Marine fossils have been found at several localities near Gunnedah. The forms listed below were found on horizons near the top of the Porcupine Formation at the following places:

Near the western boundary of portion 314, Parish of Gunnedah, County of Pottinger.

Spirifer duodecimcostata McCoy.
Spirifer sp. indet.
"*Martiniopsis subradiata*" Sowerby (plicated form).
"*Martiniopsis subradiata*" Sowerby (smooth form).
Spirifer cf. *darwini* Morris.
Astartila danai de Koninck.
Edmondia intermedia de Koninck.
Deltopecten subquinquelineatus McCoy. var. *delicatula* Fletcher.
Deltopecten leniusculus (Dana).
Platyschisma rotundata Morris.
? Pleurotomaria subcancellata Morris.

On road west of the boundary between portions 310 and 312, Parish of Gunnedah.

Terrakea fragile Dana.
Spirifer duodecimcostata McCoy.

On road between portions 313 and 315, Parish of Gunnedah, about 10 chains from their western boundaries.

"*Martiniopsis subradiata*" Sowerby.

On road south of the boundary between portions 321 and 322, Parish of Gunnedah.

Spirifer duodecimcostata McCoy (abundant).
"*Martiniopsis subradiata*" Sowerby.
Ptychomphalina morrisiana (McCoy).
Indet. pelecypod.

A band of impure limestone, underlying the horizon from which these forms were obtained yielded a doubtful specimen of *Glossopteris*.

The following forms were collected from a lower horizon in the Upper Marine sequence to the west of the scarp in portion 116, Parish of Gunnedah.

Martiniopsis subradiata var. *branxtonensis* Etheridge.
Deltopecten fittoni (Morris).
Spirifer vespertilio Sowerby.
Merismopteria ? macroptera (Morris).

Nearby, to the east of the scarp overlooking the railway line, and on a similar or perhaps lower horizon, abundant specimens of *Edmondia nobilissima* de Koninck and *Edmondia intermedia* de Koninck, together with one incomplete specimen of *Cardiomorpha gryphoides* de Koninck, were collected. The occurrence of these three forms in association to the exclusion of other forms, might suggest that the beds are of Lower Marine age, but mapping has placed them definitely with the beds which have been mapped as Upper Marine. Specimens of *Edmondia* have been collected along the Upper Marine forms from portion 314, Parish of Gunnedah, and also in a suite of fossils containing typical Upper Marine forms from portion 80, Parish of Eulah, County of Nandewar, so that the association is apparently not uncommon in the Upper Marine of the North-western Coalfield.

Overlying the Porcupine Formation there is a group of beds which it is proposed to name the Gladstone Formation. It is at least 300 feet thick and consists almost entirely of shales with odd thin bands of sandstone and carbonaceous or coaly matter. Towards the top the beds are more sandy and there are several thin bands of limestone.

The Upper Coal Measures were originally thought to consist of two groups, an upper one, which is described below under the Upper Coal Measures, and a lower one, the Gladstone Formation. However, no fossils, neither marine nor fresh water, were found in the beds comprising the Gladstone Formation.

The discovery of Upper Marine fossils near Breeza (see Part V of this series of papers) in thin beds of limestone which are developed at the top of a group of shales, makes it probable that the Gladstone Formation is of Upper Marine age. If it is not, it means that 300 feet or more of shales, representing the Gladstone Formation, have thinned out completely between Gunnedah and Breeza, and in the Breeza area up to 500 feet of shales are developed at the top of the Upper Marine sequence and are not represented in the Gunnedah district.

Shales corresponding to the Gladstone Formation probably underlie the alluvium along the railway line between Curlewis and Nea Siding and also over a considerable portion of the Booloocooroo Plains.

Upper Coal Measures. The description is confined to the upper of the two groups referred to above, which is definitely of fresh water origin. It is proposed to name this group the Black Jack Formation, because of its typical development in the vicinity of Black Jack Mountain. It has a maximum thickness of about 550 feet and consists of sandstones, shales, conglomerates, cherts and thin bands of limestone. It contains two coal seams which are of commercial grade and thin or poor quality seams are found on several other horizons. The detailed alidade survey has been concentrated mainly on this formation. *Glossopteris* and *Vertebraria* are abundant and Stonier (1890*a*) commented that at Curlewis the latter is generally vertical with respect to the stratification.

The Black Jack Formation can be conveniently divided into three zones by the two coal seams. The upper seam is being worked by the Gunnedah and Preston Extended Tunnel Collieries and has been prospected at Pryor's Well and other points. It is proposed to refer to this seam as Hoskisson's Seam and the lower seam as Melville's Seam. The latter has been prospected at Gladstone's adit, in a shaft adjacent to the Gunnedah Colliery Main Adit, in an inclined shaft near the old Preston Colliery Adit, and in Melville's Well. Hoskisson's Seam is up to 16 feet thick at some points, but the worked section is about 7 feet 6 inches thick. The coal is of high quality, the ash content being about 7% and the calorific value 13,600 B.Th.U.'s per pound. Melville's Seam is lower in grade and has a maximum thickness of about 8 feet, including bands. The ash content is about 15% and the calorific value 11,400 B.Th.U.'s per pound. However, better quality coal could be obtained from this seam by excluding certain bands.

The lowest zone of the Black Jack Formation, below Melville's Seam, is about 70 feet thick adjacent to Gunnedah Colliery. It consists of shales overlying a band of sandstone approximately 40 feet thick.

The zone between Hoskisson's and Melville's Seams consists of shales with several well marked bands of sandstone. None of the bands is in any way distinctive from the others, but outcrops of individual bands can be traced over considerable distances and form very useful beds in mapping. The zone is 190 feet thick in the Gunnedah district but at Curlewis it has thinned down to 150 feet. Outcrops are developed best in the area between the Gap and Little Sugarloaf. At Curlewis the inclined shaft to test Melville's Seam intersected 2 feet 6 inches and 1 foot of coal, 60 and 80 feet respectively above Melville's Seam. The shaft which was sunk to Melville's Seam at Gunnedah Colliery intersected 6 inches of coal, 36 feet above the seam. Near Little Sugarloaf there is also evidence of carbonaceous material at a level 35 feet above the seam. Between Little Sugarloaf and the Gap there are outcrops of weathered coaly material at several points about 70 feet above Melville's Seam.

The thickness of the beds above Hoskisson's Seam varies between 240 feet in the vicinity of Gunnedah Colliery to 300 feet in the Curlewis area. The zone contains several horizons that are worthy of particular mention.

The lowest horizon consists of a band of pale buff to terra-cotta coloured cherty claystones and shaley sandstones, which are up to 40 feet in thickness. Their development is spasmodic and they appear to owe their origin to the alteration, by igneous activity, of shales which overlie Hoskisson's Seam. In some places where the shales have been intruded by basalt the resultant rock consists of a breccia composed of cherty fragments in a basaltic cement. The main development of these beds is in the Gunnedah area south of McCosker's Adit and north and north-west of the mine workings. Their absence overlying the seam in the immediate vicinity of the main adit of the Gunnedah Colliery is no doubt due to the fact that the coal measures at this point have not been intruded by sills of dolerite. The development of these cherty beds is mainly confined to the one horizon, but local developments of similar beds do occur at odd points below Hoskisson's Seam.

Overlying the horizon of the cherty claystones is a band composed mainly of sandstone which is characterized by the presence of white quartz pebbles in certain beds. The pebbles are confined almost entirely to this band and the occurrence of abundant white quartz pebbles on other horizons within the coal measures is rare. However, exact correlation within the band is not always possible because the maximum development of the pebbles seems to be concentrated at different horizons in different places, and the thickness of the band appears to vary. Within the Gunnedah Colliery holding the band is about 100 feet thick and the base lies 50 to 60 feet above Hoskisson's Seam. On the other hand near the old Preston Mine at Curlewis, the band is only of the order of 25 feet thick and the base is only about 25 feet above Hoskisson's Seam. The occurrence of sandstone containing white quartz pebbles within the coal measures is, however, an excellent indication that the horizon in question is stratigraphically above the horizon of Hoskisson's Seam.

About 30 feet above the pebbly sandstone there is a band of chert which forms a very useful key horizon. Near McCosker's Adit within the Gunnedah

Colliery holding the band is 170 feet above Hoskisson's Seam and about 70 feet below the base of the Trias. However, care has to be taken when using this bed for correlative purposes not to confuse it with a higher band of cherts and cherty shales which occurs close to the base of the Trias. This upper band is particularly well developed west of Black Jack Mountain, in the Wondobah State Forest area, and to the south of Curlewis. It contains excellently preserved plant remains. The following forms have been recognized in specimens from Wondobah State Forest.

Glossopteris indica Schimper.
Glossopteris browniana Brong.
Glossopteris ampla Dana.
Gangamopteris cyclopteroides Feistmantel.

About half-way between the two chert bands, there is a bed of conglomerate which is developed in both the Gunnedah and Curlewis areas. Above the Gunnedah Colliery Adit the bed is 180 feet above Hoskisson's Seam and 60 feet below the base of the Trias. (At this particular point the middle band of chert is only 145 feet above the seam.) Near Preston Colliery Adit it is 170 feet above the seam and 130 feet below the Trias.

There is a very interesting local development of a thin band of impure limestone in the area west of Black Jack Mountain. It occurs close to the top of the coal measures and as far as is known it is unfossiliferous. It is concretionary in part and in some places pieces closely resemble *Stenopora* although it is apparently an inorganic structure. How far it extends westwards under the Triassic rocks it is impossible to say. Another thin band of limestone outcrops at a lower stratigraphical level on the eastern slope of Black Jack Mountain north of the Gap, but seems to have a very restricted areal development.

Silicified wood is very well developed, particularly on two main horizons. One of these is immediately overlying the sandstone with white quartz pebbles. Excellent examples from this horizon are to be found in portion 56, Parish of Black Jack, near the north-western corner of portion 39. The other horizon is close to the top of the measures to the west of Black Jack Mountain in the Parish of Gill.

Coaly matter has been reported at several horizons above Hoskisson's Seam. Carne (1908) reports the occurrence near Curlewis of a seam 5 feet thick, 100 feet above Hoskisson's Seam and a second seam composed of coal and bands 12 to 15 feet thick, a further 90 feet higher. A water bore sunk between Preston and Preston Extended Tunnel Collieries recorded coal at 55 and 85 feet above Hoskisson's Seam, but another bore near by which penetrated the same strata showed no record of coal in these positions. Professor L. A. Cotton (private report) records a thin seam of coal, 9 inches thick, 75 feet above Hoskisson's Seam. West of Black Jack Mountain in portion 13, Parish of Gill, a band of carbonaceous material occurs close to the base of the Trias.

There is a local development of andesitic breccia immediately underlying the Triassic conglomerate on Sugarloaf Mountain in portion 160, Parish of Gunnedah. The rock is obviously of a fragmentary nature and both the fragments and matrix are of similar composition. The upper contact appears to be regular but the lower contact is irregular and the underlying coal measures appear to be faulted. The bed thins considerably towards the north. The junction between the breccia and the overlying Triassic beds is very well exposed in some places. The breccia is cemented to the Triassic conglomerate and the contact resembles a chilled margin. The marginal portion of the breccia is somewhat altered and iron-stained but microscopical examination shows that it is composed of brecciated material similar to the main mass. The alteration, iron-staining and cementation to the Triassic conglomerate may be the result of leaching by ground waters moving along adjacent to the contact with redeposition of iron oxides to give a banded appearance. The bed is probably a flow breccia which was erupted about the close of the Permian era. The only other outcrop of similar material in the area is a small isolated one on the top of a hill composed of coal measures in M.L. 5, Parish of Gunnedah. If it were not for the fragmentary nature of the material on Sugarloaf Mountain it would be natural to group it with the Tertiary intrusives and classify it as a sill. However, in order to do this, it would be necessary to explain the brecciation as being due to movement during solidification.

Several examples of intrusive tuffs have been referred to by Browne (1929) and Mr. E. J. Kenny (unpublished report) records the occurrence of intrusive rocks which microscopical examination show to have the composition and texture of arkoses. However, it would probably be even more difficult to explain the mechanics of the intrusion of a coarse breccia, especially if a considerable time break be postulated between the deposition of the intruded sediments and the period of the intrusion.

Triassic.

The Triassic beds mapped consist of conglomerates and sandstone. Shales, several hundred feet thick, have been recorded by Mr. E. J. Kenny (unpublished report) in bores which have been sunk for water in the vicinity of Haystack Mountain, to the west of the area mapped.

The conglomerates and sandstones have been named the Digby Beds by Kenny (1928). The basal beds consist of conglomerates and are characterized by the presence of abundant pebbles of red jasper. The conglomerates differ sufficiently from other conglomerates which outcrop in the district to make them readily recognizable and form a very valuable horizon for mapping purposes, enabling the upper limits of the Permian System to be delineated accurately. They are noteworthy for the presence in them of boulder beds, many of the boulders being more than a foot in diameter. The boulder beds are very well developed to the west of Black Jack Mountain in the Parish of Gill. The coarse conglomerates grade upwards through fine conglomerates and sandstones with pebbly bands, into the overlying sandstones. They vary in thickness between 20 and 100 feet, and average about 30 to 40 feet.

The sandstones are generally thinly bedded and outcrop over wide areas, being considerably thicker than the conglomerates. Their upper limits were not mapped during the present survey.

Thin beds of fine-grained rhyolite breccia and decomposed volcanic breccia have been found in a few localities, the main ones being in the Parish of Digby and in Wondobah State Forest.

No fossils were found in the Digby Beds anywhere in the area, and following Kenny they have been classified as Triassic. They are similar to beds in neighbouring areas to the south-east which have been previously classified as Triassic.

Tertiary.

The Tertiary rocks are entirely of igneous origin and comprise olivine and analcite dolerites and olivine and nepheline basalts. They occur as sills, dykes and flows, and form cappings to most of the high hills in the district. The cappings mostly consist of fairly coarse-grained dolerites and were probably intruded as sills under a thin cover of sediments which have been subsequently eroded. Sills have been found intruding all formations in the district except the Upper Marine. In some places the sills may have passed laterally into flows.

The disposition of the sills appears to be related to the topography. Along the main portion of Black Jack Mountain they are common in the Triassic rocks but relatively little developed through the coal measures. The dolerite reaches its maximum development in the vicinity of King Jack Trignometrical Station where altogether there must be a total thickness of the order of 1,000 feet. East and west of Black Jack Mountain the coal measures have been extensively intruded by sills of dolerite. These sills have already had considerable influence on the development of the coal resources of the district and will continue to do so in the future. Beyond the northern limits of the outcrops of the Triassic rocks along Black Jack Mountain, it is found again that the coal measures have been affected by igneous activity. Because the intrusion of sills depends on the ability of the igneous material to lift the overlying strata and hence on their thickness, the disposition of the dolerite sills in relation to the present topography would indicate that relatively high ground in Tertiary time occupied approximately the same positions as the present areas of relief.

In many places the sills have broken through from one level to another, thus giving a complex shape to the intrusive mass. Dolerite and basalt talus tends to be scattered over the hill slopes, often completely obscuring outcrops of sediments. The combination of the above effects renders accurate mapping of boundaries very difficult and in some places impossible. No attempt has been made to map many isolated outcrops of Triassic sandstone which occur along the higher levels of Black Jack Mountain.

Dykes occur as a network in some areas and probably formed the main feeders by which the sills were intruded. Professor L. A. Cotton (private report) gives the dominant direction of the dykes as south-westerly, with a second direction of minor importance about N. 20 W. and a third direction of still lesser importance trending slightly north of west. The dykes are probably more numerous in areas where sills or flows of dolerite are present.

West of the area shown on the map (Plate XVI) there is a widespread development of olivine and analcite dolerites which have been mapped as Garrawilla (Jurassic) flows. When examined microscopically they are found to be identical with typical Tertiary dolerites. It is considered that it would be preferable to classify most of these rocks as Tertiary sills as originally proposed by Kenny (1927) rather than as Jurassic flows.

Tertiary to Recent.

These deposits are confined to the alluvium along the Namoi and Mooki Rivers and their tributaries. The main development is in the Booloocooroo Plain and the area to the east, across to the Mooki River.

The alluvium consists of "black soil," red clay, sandy clay, sands and gravels. East of the belt in which the Upper Marine beds occur the alluvium may be largely underlain by Werrie Basalts.

STRUCTURAL GEOLOGY.

The structural geology is relatively simple when compared with that of the sections of the North-western Coalfield described previously in this series of papers. The Gunnedah-Curlewis district is wholly situated to the west of the Hunter-Mooki zone of thrust-faulting. The structure consists of minor folding and faulting which has been superimposed on a general dip to the south-west.

Structure contours on the base of the Upper Marine Series show that a small basin exists in the position where the *Glossopteris*-bearing shales are developed near Gunnedah. This relationship could be explained in either one of two ways. First folding may have commenced at the time the shales were being deposited and they could represent a local development in a small basin formed in this manner. If this were so it might have been expected that the folding would have tended to persist to some extent into Upper Marine time and be reflected in a local thickening of the overlying strata. However, as the overlying Upper Marine beds have been removed to a large extent in this section by erosion, it was not possible to obtain evidence either for or against this contention. Secondly, it may be that the position of a small basin developed during later folding may have been influenced so as to be located where there was a local development of underlying sediments.

The detailed alidade survey has disclosed minor folding in which both the Triassic and Upper Coal Measures have participated, and which a reconnaissance survey would have failed to reveal. If suitable key beds could be found in the Triassic beds further west, similar detailed surveying may disclose minor folding of a like nature. The apparent simplicity of structure in many of the areas occupied by Triassic rocks is probably due to the lack of outcrops of suitable key beds and sufficient detailed survey work.

The most interesting structure in the Triassic rocks is an undulating anticlinal zone which has been superimposed on the general dip and accounts for the zone of isolated outcrops of the Upper Coal Measures to the west of Black Jack Mountain in the Parish of Wondobah. This zone continues northwards into the Parish of Gill and south-eastwards into the Parish of Digby.

Many of the folds and small faults which exist in the district are certainly younger than Triassic Digby beds. Some, at least, of the faults appear to be associated with the intrusion of the Tertiary dolerites.

Acknowledgements.

I was assisted on the geological survey by Mr. J. C. Lloyd, B.Sc., who was responsible for the instrumental work and many helpful discussions with him on points raised during the progress of the work are gratefully acknowledged. I am indebted to Mr. H. F. Whitworth, M.Sc., Curator of the Mining Museum, for the petrological determinations ; to Dr. A. B. Walkom, Director of the Australian Museum, for determinations of the plant fossils ; and to Mr. H. O. Fletcher, Palæontologist of the Australian Museum, for determinations of the marine fossils. I also wish to express my thanks to Mr. J. E. Lancaster, Under-Secretary for Mines, and Mr. C. St. J. Mulholland, B.Sc., Government Geologist, for permission to publish this paper.

Summary.

The Permian sequence comprises Lower Marine lavas and subordinate fresh water sediments, Greta Coal Measures (?), Upper Marine Series and Upper Coal Measures. It is overlain conformably by Triassic conglomerates and sandstones. Sills, dykes and flows of Tertiary dolerite form extensive outcrops and there are also extensive alluvial areas. The general dip is south-westerly and on it minor folding, which has affected both Permian and Triassic beds, has been superimposed.

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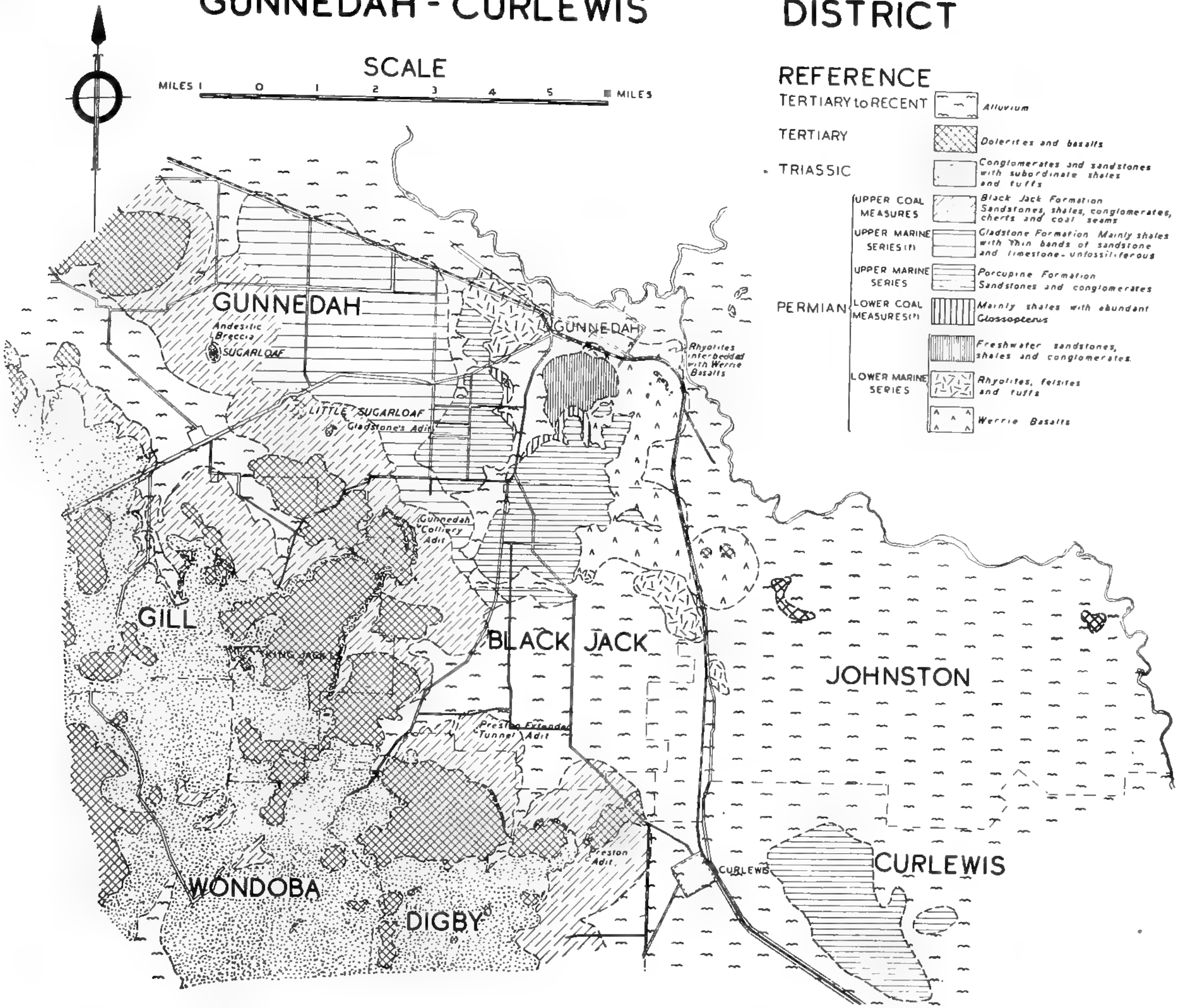
Journal Royal Society of N.S.W., Vol. LXXXII, 1948, Plate XVI

GEOLOGICAL MAP GUNNEDAH - CURLEWIS DISTRICT



GEOLOGY OF THE NORTH-WESTERN COALFIELD, N.S.W.

PART V. GEOLOGY OF THE BREEZA DISTRICT.

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With Plate XVII.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION.

The area covered by this paper extends from the Gunnedah-Curlewis district (Hanlon, 1948), which it adjoins on the north, to about four miles south of Breeza. The survey was in the nature of a detailed reconnaissance. Spot heights on the base of the Triassic between Curlewis and Nea Siding were established by resections and an alidade traverse was made from the railway line in the vicinity of Breeza, across to the Triassic conglomerate near Watermark Trigonometrical Station, and thence to the north-western corner of portion 144, Parish of Breeza, County of Pottinger, where Upper Marine limestones outcrop.

TOPOGRAPHY AND ACCESS.

Breeza is situated on the North-western Railway line, being 269 miles from Sydney and 953 feet above sea level. Access by road is good, although many of the roads are not gravelled and are impassable after any appreciable rain. The area is wholly situated within the County of Pottinger.

The Mooki River, which flows immediately to the east of Breeza, is the main stream in the district. It is a tributary of the Namoi River, which it joins near Gunnedah. Other streams are only insignificant.

The district is bounded on the east and south by alluvium, and large sections of the north and west are also alluviated. Relief is moderate, the highest points being Cockroft and Watermark Trigonometrical Stations, 1,885 and 1,678 feet above sea level respectively.

GEOLOGY.

The geological formations of the district comprise the following, which will be described in order, commencing with the oldest:

- Tertiary to Recent alluvium.
- Tertiary Igneous Rocks.
- Triassic.
- Permian.
  - Upper Coal Measures.
  - Upper Marine Series.

Permian.

Only the Upper Coal Measures and Upper Marine Series are represented in the Breeza district. The Lower Marine lavas which are so well developed further north around Gunnedah and Boggabri do not outcrop, but the Werrie

Basalts (Lower Marine) may underlie a large portion of the Breeza Plains to the east.

Upper Marine Series. Only the upper beds are exposed and it is only thin limestone bands which form recognizable outcrops. From bore records it appears that the underlying beds are composed mainly of shales. These shales form very poor aquifers and supplies of water obtained are almost invariably salt.

In the Parish of Breeza, within Portion 144 and the south-western corner of Portion 155, thin bands of fossiliferous limestone outcrop. The following forms were found:

Aviculopecten multicostatus Fletcher.
Platyschisma ocula Sowerby.
Astartila danai De Kon.
Mytilus cf. *bygsbyi* De Kon.
Deltopecten ? fittoni (Morris).
? Notomya cuneata Sowerby.
? Stutchburia costata (Morris).
? Spirifer sp.
Pelecypod. (Resembles an undescribed form found low in the Branxton Stage of the Upper Marine Series.)

It is proposed to name the shales and interbedded limestones the Watermark Formation because its typical development is in the neighbourhood of the railway platform and trigonometrical station of that name. It is in no way comparable with the fossiliferous Upper Marine sandstones and conglomerates (the Porcupine Formation) in the Gunnedah-Curlewis district (Hanlon, 1948). It is considered unlikely that such a complete facies change would take place between Nea Siding, adjacent to which the Porcupine Formation outcrops, and Watermark, a distance of only three miles. This probably means that the Watermark Formation represents a subsequent development to the Porcupine Formation and suggests that it should be correlated with the Gladstone Formation of the Gunnedah district. As stated previously (Hanlon, 1948), the Gladstone Formation is unfossiliferous and was formerly considered to be part of the Upper Coal Measures sequence. It was the suggested correlation with the Watermark Formation which made it likely that the Gladstone Formation might be of Upper Marine Age. Otherwise it is necessary to postulate that in Upper Marine time the 500 feet of shales making up the Watermark Formation either lensed out completely or passed laterally into a thinner group of sandstones and conglomerates (Porcupine Formation), and that subsequently in Upper Coal Measures time, 300 feet or more of shales in the Gunnedah district (Gladstone Formation) lensed out completely in the opposite direction.

Upper Coal Measures. It is considered that the Upper Coal Measures sequence in the Breeza district represents the south-easterly continuation of the Black Jack Formation which was mapped in the Gunnedah-Curlewis district (Hanlon, 1948). In the northern portion of the area mapped the sequence is the same as that of the Black Jack Formation in the type area and consists of sandstones, shales, conglomerates, cherts and coal seams. Besides the species of *Glossopteris* which have been collected in other parts of the North-Western Coalfield, specimens of *Glossopteris conspicua* Feist. were found in cherty shales close to the base of the overlying Triassic conglomerates in Portion 205, Parish of Curlewis. Good specimens of the basal end of the stem of *Phyllotheca australis* Brong. were also collected from this horizon.

Further south in the vicinity of Watermark Trigonometrical Station the facies have altered somewhat and part of the upper portion of the sequence is missing. The topmost bed in the coal measures near Watermark T.S. is about ten feet thick and consists of shales with cherty bands. It overlies eighty feet of sandstones with bands of white quartz pebbles which in turn overlie terra-cotta coloured cherty claystones. It is considered that the last two zones correspond to similar ones in the Gunnedah district (Hanlon, 1948). Whether the overlying cherty shales correspond to the middle or upper band of cherts from the Gunnedah-Curlewis area it is not possible to say. However, which ever band it represents there are strata of the order of 150 feet which are present in the Gunnedah-Curlewis district and are missing from the vicinity of Watermark. The beds appear to be conformable and conditions favour non-deposition of the missing beds rather than their deposition and subsequent erosion.

Coal has been prospected in portions 123 and 89 in the Parish of Breeza and has also been struck in several wells and bores sunk for water. The logs of some of the bores suggest that Hoskisson's Seam is tending to split towards Breeza or that other seams are developed locally on adjacent horizons to it. It is considered that the seam prospected at Breeza is on or about the horizon of Melville's Seam. Associated with it there is a marked development of beds of conglomerate, the pebbles being composed mainly of acid lavas. It is a distinct change of facies compared with the Gunnedah district. Harper (1913) reported on the quality of the coal in portion 123.

Triassic.

The Triassic beds mapped consist of conglomerates and sandstones similar to those described in the Gunnedah-Curlewis district. In the northern section of the area in the Parish of Curlewis, the beds form a characteristic line of cliffs. However, to the south-west of Nea Siding and west of Breeza the conglomerates form poor outcrops, the positions the beds occupy being indicated by the occurrence of very abundant jasper and quartzose pebbles. Actual outcrops of beds of conglomerate are relatively few.

Tertiary Igneous Rocks.

The Tertiary rocks comprise dolerites and basalts and their modes of occurrence are similar to those in the Gunnedah-Curlewis district.

The most noteworthy feature is the occurrence of a sill in the Breeza-Watermark area which is developed at, or slightly below, the horizon which Hoskisson's Seam would occupy if developed. Its position in relationship to beds of buff and terra-cotta coloured cherty shales which underlie sandstones with white quartz pebbles is similar at all points in which the beds have been examined. To the north of Watermark Trigonometrical Station a breccia composed of fragments of chert in a basaltic cement is common.

According to local reports one well sunk in portion 8, Parish of Nea, has the western side formed by a vertical wall of rock (dolerite ?), while the eastern side consists of coal measures with a low dip, including coal on three horizons (splits of Hoskisson's Seam ?). This suggests that the dolerite is in the form of a dyke, but further west the same mass obviously underlies a band of sandstone with white quartz pebbles, and the intrusion must be concordant in some places and transgressive at others.

Tertiary to Recent.

Alluvium occupies a large proportion of the area mapped. It completely surrounds the area on the east and south and forms large sections to the north and west. It is of the " black soil " variety and on the north and east is probably underlain by Upper Marine shales and Werrie basalts (Lower Marine). Eastwards it extends across the Breeza Plains until it reaches the Carboniferous hills to the east of the Mooki Thrusts (Carey, 1934).

STRUCTURAL GEOLOGY.

As in the Gunnedah-Curlewis district, the structures are relatively simple when compared with the zone of pronounced folding and thrust faulting further to the east.

The main dip is generally in a south-westerly direction except in the Watermark area. Here the structure consists of a dome or a very pronounced nose. It is closed to the west, south and north-east, but to the north it is obscured by alluvium and may or may not be completely closed. It is proposed to name the structure the Watermark Dome. Upper Marine beds outcrop in the core of the dome. North-easterly, southerly and westerly dips occur in the overlying Upper Coal Measures. The folding has affected the Triassic as well as the Permian. However, as described above, much of the topmost portion of the Upper Coal Measures sequence is missing in this area, which indicates that some of the folding was pre-Triassic.

ACKNOWLEDGEMENTS.

I was assisted on this survey by Mr. J. C. Lloyd, B.Sc., and many helpful discussions with him during the course of the work are gratefully acknowledged. I am indebted to Dr. A. B. Walkom, Director of the Australian Museum, for the determinations of the fossil plants, and to Mr. H. O. Fletcher, Palæontologist to the Australian Museum, for the determinations of the marine fossils. I wish especially to thank Mr. J. M. Clift, of Giligulgul, Queensland, for making available to the writer a collection of marine fossils made by him in the Breeza district. I also wish to express my thanks to Mr. J. E. Lancaster, Under-Secretary for Mines, and Mr. C. St. J. Mulholland, Government Geologist, for permission to publish this paper.

SUMMARY.

Only the upper part of the Permian sequence, comprising the Upper Marine Series and Upper Coal Measures, outcrops in the area. It is overlain by Triassic conglomerates and sandstones. The beds have been intruded by Tertiary dolerites and there are also extensive areas of alluvium. There is a general dip to the south-west except in the Watermark area, where there is a dome which was formed partly in pre-Triassic and partly in post-Triassic time.

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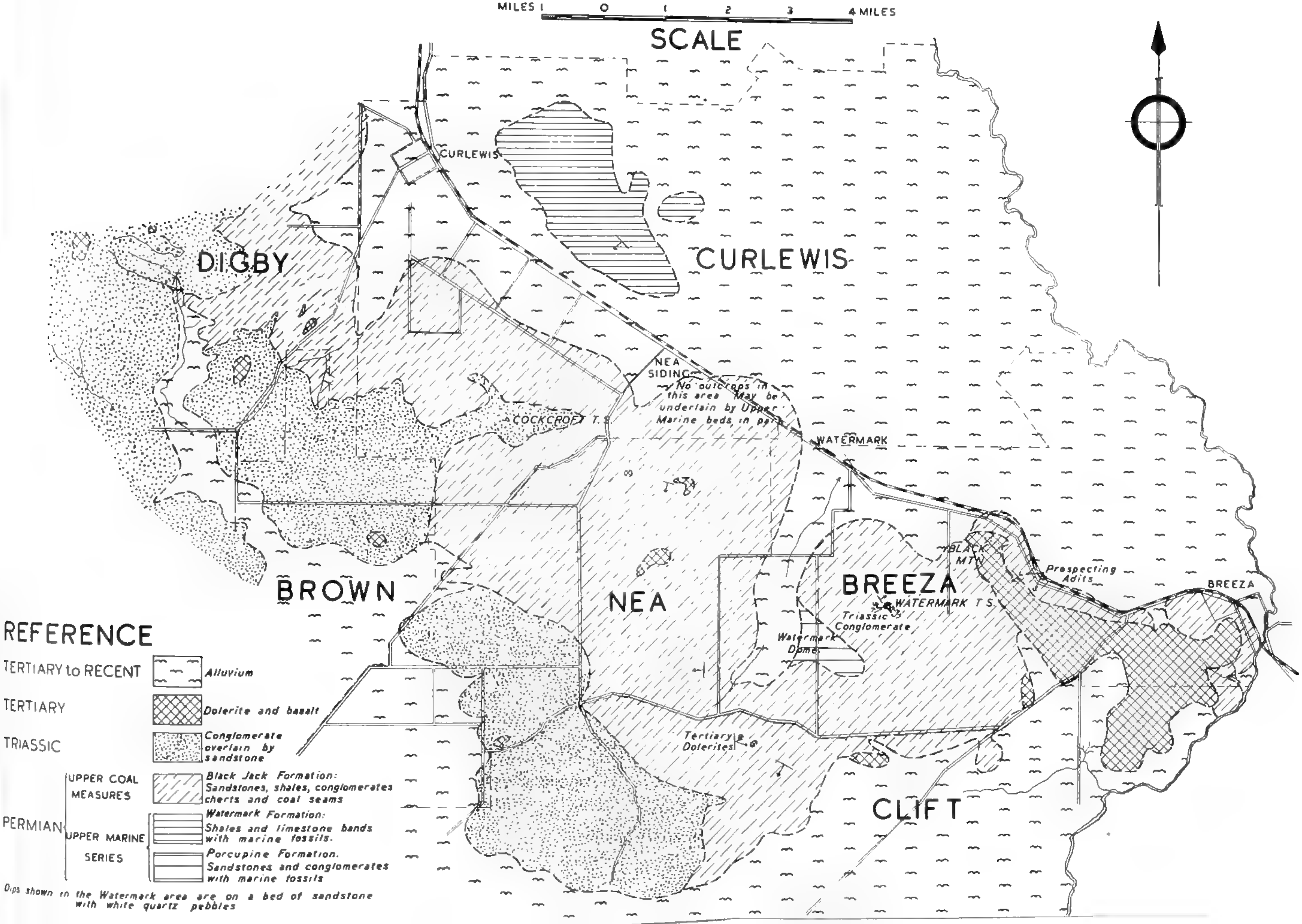
GEOLOGICAL MAP BREEZA DISTRICT



GEOLOGY OF THE NORTH-WESTERN COALFIELD, N.S.W.

PART VI. GEOLOGY OF SOUTH-WESTERN PART OF COUNTY NANDEWAR.

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Geological Survey of New South Wales.

With Plate XVIII.

(Presented by permission of the Under Secretary for Mines.)

Manuscript received September 23, 1948. Read October 6, 1948.

INTRODUCTION.

The area geologically surveyed comprises about 350 square miles of territory in the south-western part of the County of Nandewar. It adjoins the main section of the North-western Coalfield along the Namoi River in the neighbourhood of Gunnedah (Hanlon, 1948*a*). Although practically unprospected and hitherto not included within the State's likely coal-bearing areas, the survey has shown that this area represents a potential addition to our coal reserves. It continues the survey of a belt of country in which the eastern margin of the Permian sediments in the North-western Coalfield is situated. This belt extends from the Murrurundi-Willow Tree district (Hanlon, 1947*b*, 1947*c*, 1947*d*), through the Werrie Basin (Carey, 1934, 1935, 1937), to the Gunnedah-Manilla district (Lloyd, 1933). The area mapped adjoins and to some extent overlaps the Gunnedah-Manilla district. The boundaries of the Carboniferous and Devonian rocks south of Round Hill, shown on Plate XVIII, have been taken from the map of the above area.

TOPOGRAPHY AND ACCESS.

The North-western Railway passes to the west of the area through Gunnedah and Boggabri on the Namoi River, 295 and 320 miles from Sydney respectively.

Access by road is good during dry weather, but as many of the roads cross areas of black soil, they become impassable after appreciable rain. Roads connect with Gunnedah and Boggabri on the west and across the range with Tamworth, Manilla and Barraba on the east.

The area is one of medium relief and lies between the valley of the Namoi River on the south and west, and a line of hills to the east, which joins the Nandewar Range further north. The northern boundary is formed by Maules Creek, a tributary of the Namoi River. Much of the area consists of wide areas of alluvium which slope gently towards the Namoi River. Tributaries of the Namoi River, other than Maules Creek, are insignificant.

Gunnedah and Boggabri, which are situated adjacent to the Namoi River, are 876 and 823 feet above sea level respectively. The highest points in the area are situated within Vickery and Leard State Forests and at Mount Goonbri, being 500 to 800 feet above the plain level. The line of hills to the east are somewhat higher and appear to rise northwards towards the Nandewar Mountains.

GEOLOGY.

The geological formations comprise the following:

- Tertiary to Recent alluvium.
- Tertiary Igneous Rocks.
- Permian
    - Nandewar Group.
    - Boggabri Volcanics.
- Carboniferous
    - Upper Kuttung Series.

The rocks will now be described in detail commencing with the oldest.

Carboniferous.

The Carboniferous rocks have not been mapped in detail because the survey was concerned primarily with the Permian beds. The Carboniferous-alluvium boundary south of the latitude of Boggabri has been taken from the map of the Gunnedah-Manilla district (Lloyd, 1933).

The rocks outcrop along the eastern boundary of the area surveyed and belong to the Upper Kuttung Series. They consist of acid lavas, tuffs and conglomerates, the lavas comprising rhyolites, porphyritic rhyolites (Lloyd, 1933), felsites, andesites and pitchstones.

A considerable area to the north of Boggabri has been classed as Carboniferous on old maps in the Department of Mines, but these rocks have now been grouped with the Boggabri volcanics described below.

Permian.

The Permian rocks comprise a group of sedimentary beds and a group of lava flows. It is proposed to name the lava flows the Boggabri Volcanics, because their maximum development is adjacent to and north of that town. The sediments have been called the Nandewar Group since they are typically developed within the County of Nandewar.

Boggabri Volcanics. They comprise flows which are considered to be of Lower Marine age because of their similarity to flows, west of the Namoi River at Gunnedah, which appear to form part of the Lower Marine sequence. They have been intruded by later, probably early Tertiary, alkaline rocks, which may be related to the Nandewar Mountain intrusives. The later intrusives have been included with the Boggabri Volcanics for mapping purposes because in the time available no satisfactory separation of the two groups of igneous rocks could be made. Such a separation would entail a considerable amount of careful collecting and the study of many rock sections. The Tertiary alkaline rocks collected are described below under the Tertiary volcanics.

The outcrops of the Boggabri Volcanics consist almost entirely of acid lavas and tuffs, the lavas comprising rhyolites, trachytes, andesites and basalts. This phase of the Lower Marine volcanic activity is much more extensively developed near Boggabri than the corresponding phase at Gunnedah. On the other hand the Werrie Basalts, which are interbedded with the lavas and tuffs and predominate to the south and west of Gunnedah, do not form conspicuous outcrops in the Boggabri area. Saint Smith (1911) records decomposed amygdaloidal basalt on the western side of the Namoi River in M.L. 3, Parish of Boggabri, County of Pottinger.

Nandewar Group. It is proposed to subdivide the Nandewar Group into the Wean formation and the overlying Vickery Conglomerate. Both formations are typically developed within the Parish of Vickery, the Vickery Conglomerate especially so within the State Forest of that name.

The Wean formation is of fresh water origin and contains abundant impressions of *Glossopteris browniana* Brong, *Glossopteris ampla* Dana, *Glossopteris tortuosa* Zeiller, and *Glossopteris* sp. *Noeggerathiopsis hislopi* Feistmantel was also found. As far as the formation is exposed it consists of shales, sandstones and conglomerates with coal seams and is at least 350 feet thick. The shales are ferruginous in places and contain bands of concretionary ironstone. A coal seam 7 feet 10 inches thick (including a two-inch band near the middle) was struck at a depth of 86 feet in a well in portion 12, Parish of Vickery. The seam was lying almost horizontally. The ash content was 12·9% and the calorific value 12,487 B.Th.U.'s per lb. on a moisture-free basis. Many bores for water in the Parishes of Brentry, Vickery, Boggabri, Leard, Bollol and Berrioye have struck coal. However, as the bores were all sunk with percussion plants and the logs were provided by the drillers, any information as to the thickness or quality of the seams is unreliable.

The Vickery Conglomerate consists of pebbles of medium size, although in places boulders up to a foot across occur. Most of the pebbles have been derived from acid lavas. Sandy or shaley facies are developed only to a minor extent. The Vickery Conglomerate is at least 530 feet thick, and in the absence of fossil evidence it is impossible to state definitely that it is not of marine origin. Besides its development in Vickery State Forest, it is also well developed in the higher portions of Leard State Forest and on Mount Goonbri underlying the dolerite capping.

Correlation. In any attempt at correlating the beds with the Permian sequence of the type area in the Hunter Valley, the absence of any marine fossils is a serious difficulty. This leaves as bases for correlation only the plant fossils, lithological sequence, the most likely relationship of the group to known Permian strata in adjacent areas and the rank of the coal. At the best these can be only indications but, provided the evidence is not contradictory, may provide a reasonable tentative correlation.

There are three possible coal-bearing fresh water zones in the Permean sequence with which the Nandewar Group could be correlated, that is, of course, provided it is not considered a fresh water equivalent of beds which are elsewhere only known to be marine. These are the Upper and Lower Coal Measures (Clarke, 1870 ; David, 1907), and the basal fresh water portion of the Lower Marine series (Hanlon, 1947*b*, 1947*c*, 1947*d*). It is considered impossible to differentiate between the Upper and Lower Coal Measures by means of the flora with any certainty. Although *Gangamopteris* is more plentiful than *Glossopteris* at some places in the Lower Coal Measures, this is not always the case. On the other hand *Glossopteris* appears definitely to be subordinate in the fresh water portion of the Lower Marine. *Gangamopteris cyclopteroides* and *Phyllotheca australis* have been recorded from these beds in the Murrurundi district (Hanlon, 1947*d*) and Carey (1935) records *Noeggerathiopsis hislopi*, *Gangamopteris cyclopteroides*, *Gangamopteris* sp. *Glossopteris* cf. *browniana* and *Palæovittaria McCarthyi* from them in the Werrie Basin. It is considered that the abundance of *Glossopteris* in the Nandewar Group would render its correlation with the basal fresh water portion of the Lower Marine unlikely and that it is at least as young as the Lower Coal Measures.

The lithological sequence differs markedly from that of the Upper Coal Measures in the adjacent Gunnedah area. It could be, of course, that the Vickery Conglomerate represents a coarse marginal phase laid down close to the edge of the Upper Coal Measures basin but this is considered doubtful. In the Breeza area (Hanlon, 1948*b*) conglomerates composed largely of pebbles of acid lava are developed above and below the horizon of the coal seam close to the base of the Upper Coal Measures sequence. However, in the area under consideration the Vickery Conglomerate is apparently developed several hundred feet above the horizons of the coal seams. The closest resemblance which the sequence bears to that of coal measures in other parts of the North-western Coalfield is with Werris Creek (Carne, 1913, 1914 ; Benson, 1920 ; Carey, 1934, 1935 ; Hanlon, 1946), where the measures consist of 350–400 feet of shales, sandstones, conglomerates and coal seams, overlain by 50–100 feet of conglomerates. Here, too, the conglomerate pebbles consist largely of acid lavas, although quartzite is also common. Carey (1935) recorded an abundant *Glossopteris* flora from these beds, plants collected including *Glossopteris browniana*, *Glossopteris indica*, *Glossopteris ampla*, *Noeggerathiopsis hislopi*, *Phyllotheca australis* and *Phyllotheca* cf. *etheridgei*, and correlated the beds with the Upper Coal Measures. However, as these beds overlie conformably the Werrie Basalts, which are now known to be of Lower Marine age (Hanlon, 1947*b*, 1947*c*, 1947*d*) it is considered that they are more likely to belong to the Lower Coal Measures, as originally suggested by Carne (1913).

At Ashford, too, the Permian sequence comprises coal-bearing beds overlain by conglomerates (Pittman, 1896 ; Hanlon, 1947*a*). The Ashford Measures are also thought to be of Greta age.

Harper (1909) reported Upper Marine fossils from 14 miles east of Narrabri. It is expected that future work in this area north of Maules Creek may show that the Upper Marine beds overlie the northerly continuation of the Nandewar Group. If this be so it would mean the latter should be correlated with the Lower Coal Measures, which agrees with the suggested correlation of the Nandewar Group with the measures at Werris Creek.

Dr. J. A. Dulhunty has kindly examined microspores from a sample of coal from the Parish of Vickery. He stated (private communication) that : " I was unable to find any of the types which usually characterize the Greta . . . the spore assemblage in the coal in question certainly appeared more like Upper Coal than that of Maule's Creek and Werris Creek materials which could be Greta from their spore contents." It is interesting that although the spore content of the coal in the Wean Formation favours classying it as belonging to the Upper Coal Measures the spore content of the coals at Maule's Creek and Werris Creek, of whose age there is some doubt, are consistent with a Greta age. It is with these two groups of coal measures that the field-work suggests the Wean formation should be correlated.

The rank of the Permian coals has often been regarded as useful in assisting correlation of coals from different districts. Jones (1939) quotes the following carbon ratios for the Northern Coalfield.

Greta	55·56
Tomage	60·49
Newcastle	61·13

However, the carbon ratios are of no value in differentiating between coals occurring in the Lower and Upper Coal Measures in the North-western Coalfield. Dealing first with the Upper Coal Measures, the carbon ratios of the Upper or Hoskisson's Seam at Gunnedah Colliery is 59·8 and at Preston Extended Tunnel Colliery 59·3. However, individual plies vary between the limits 67·4 and 53·7. The Lower or Melville's Seam at Gunnedah Colliery has a carbon ratio of 59·8 and individual plies vary between 61·2 and 56·7. The seam prospected at Breeza has a carbon ratio of 58·7 (Harper, 1913). Compared with the figures quoted above by Jones, it will be seen that the average carbon ratios lie between those of the Newcastle and Greta Coal Measures, while the upper and lower limits are higher than the figures for the Newcastle Measures and lower than those for the Greta Measures respectively. Considering the figures for the Lower Coal Measures a large variation is again found. The carbon ratios of the coal seam at Willow Tree are given below. The analyses on which the first five figures are based are quoted by Raggatt (1938). The last two figures are based on analyses supplied by the lessees.

Grab sample from dump by L. J. Jones	63·5
Picked sample from dump	56·3
Upper four feet of seam	56·3
Lower five feet of seam	60·9
Two pieces of bright coal dug out under water in bottom of shaft	52·7
Full section of seam—16 feet	63·8
Do.	51·8

The carbon ratios of the coal from the Werris Creek Colliery is 67·2 and varies between the limits of 59·9 and 68·8.

The carbon ratio of the coal from the well in portion 12, Parish of Vickery, is 63·8. Although this figure is much higher than those for the Greta Measures and is more closely related to those for the Newcastle Coal Measures in the Northern Coalfield, it is similar to or less than those for known Greta coals in the North-western Coalfield.

To sum up, it may be stated that the lithological sequence and possible relationship of the beds to the Upper Marine further north favour correlating the Nandewar Group with the Lower or Greta Coal Measures. On the other hand the spore contents rather favour correlation with the Upper Coal Measures. The fossil flora and carbon ratio of the coal do not favour correlating the beds with either group of coal measures rather than the other, but are not inconsistent with what might be expected in beds of Greta age. It has therefore been decided to assign the Nandewar Group tentatively to the Lower or Greta Coal Measures. The beds were probably laid down in a narrow trough whose main axis trended approximately north-north-west. The Lower Marine lavas to the west in the vicinity of Boggabri and Gunnedah were probably not entirely submerged beneath the waters of the Greta lake and may even have been undergoing some erosion.

Tertiary Igneous Rocks.

The Tertiary igneous rocks comprise the alkaline intrusives referred to above under the Boggabri Volcanics, together with some occurrences of dolerite and basalt.

The alkaline intrusives comprise rhyolites, trachytes, trachyandesites, andesites and pitchstones. They appear to be confined almost entirely to the area within which the Lower Marine flows outcrop and were probably intruded into a zone of weakness along a structural high. Jensen (1907) referred to acid igneous rocks intruding the Permian in the neighbourhood of Boggabri and it was probably in connection with these later igneous rocks that he noticed the evidence of their intrusive nature. This is well shown in portion 28, Parish of Leard, where rhyolite can be seen intruding *Glossopteris*-bearing shales which form part of the Wean formation.

The dolerites and basalts form only restricted outcrops, the main occurrences being on Mount Goonbri and between Maules and Back Creeks. The basalt outcrops shown on Yarrari Mount and Round Hill are taken from the map by Lloyd (1933). There is a small outcrop of amygdaloidal basalt in portion 13, Parish of Bollol, adjacent to the fault which forms the boundary between the Carboniferous and the Permian. Bores sunk through the alluvium in the vicinity of the northerly continuation of the line of the fault have also struck basalt.

Tertiary to Recent.

Sedimentary deposits of these ages are represented almost entirely by the alluvium of the Namoi River and its tributaries and occupy a large part of the area mapped. It is of the " black soil " type and in places it is many miles in width. Over portion of the area it may be underlain by Werrie Basalts which fail to outcrop because of the relative ease with which they weather.

STRUCTURAL GEOLOGY.

A large proportion of the region is obscured by alluvium and throughout much of the lower lying part of the area occupied by the Nandewar Group it is not possible to measure dips in the beds. However, such dips as were measured indicate that the central and western zones of the Nandewar Group form simple structures and have low dips or are lying almost horizontally. On the other hand, the eastern zone near the junction with the Carboniferous rocks is folded into a tight syncline, dips varying between 55° and almost 90°. The axis of the syncline trends north-north-west, parallel to the Carboniferous boundary. There is no doubt that this boundary is in the nature of a faulted junction. The tight folding and the dragging up of the beds of the Nandewar Group west of the fault until they are dipping almost vertically favour classifying the fault as a thrust. Lloyd (1933) mapped a fault further to the east which the writer considers to be a thrust. This means that north of the Namoi River there are two parallel thrust faults only a few miles apart, the same conditions as Carey (1934) found south of the Namoi River in the Werrie Basin. The fault mapped by Lloyd (1933) is probably the northerly continuation of Carey's eastern thrust and the one referred to above a continuation of his western thrust. Carey shows his eastern and western thrusts joining in the Babbinboon area. It seems likely that the western thrust bifurcates near where it is met by the Babbinboon fault, the main branch paralleling the portion of the eastern thrust which strikes nearly east and west and then swinging away more to the north, the other branch joining the eastern thrust as mapped by Carey.

Whether there is further faulting west of the western thrust it is not possible to say owing to the widespread alluvium, the lack of outcrops showing measurable dips and the absence of key horizons which can be mapped in the central and western zones.

The position of the synclinal area occupied by the Nandewar Group has been determined by the position of the original trough formed in Greta time. West of this trough the Lower Marine lava flows occur along what was probably a structural high even as early as that time. On the western side of the Namoi River the Greta sediments are either not developed or else occupy very restricted and isolated basins. At most points the Lower Marine lava flows are directly overlain by either Upper Marine or Upper Coal Measures sediments.

ACKNOWLEDGEMENTS.

I was assisted on this survey by Mr. J. C. Lloyd, B.Sc., and many helpful discussions with him during the course of the work are gratefully acknowledged. I am indebted to Dr. H. B. Walkom, Director of the Australian Museum, for the determinations of the fossil plants, and to Mr. H. F. Whitworth, M.Sc., Curator of the Mining Museum, for the petrological determinations. I also wish to express my thanks to Mr. J. E. Lancaster, Under-Secretary for Mines, and Mr. C. St. J. Mulholland, Government Geologist, for permission to publish this paper.

SUMMARY.

The area comprises a synclinal zone of Lower Coal Measures bounded on the west by Lower Marine lavas, which form a structural high, and on the other side

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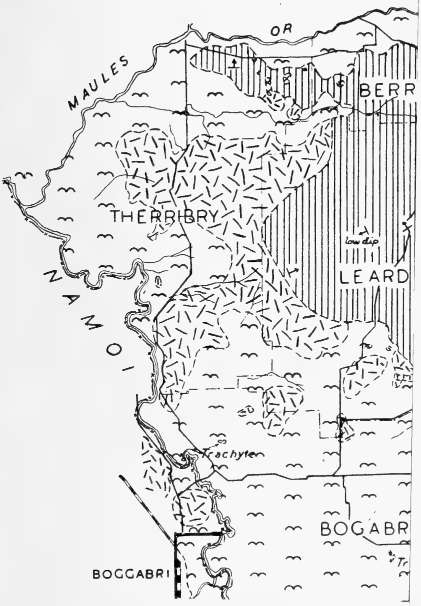
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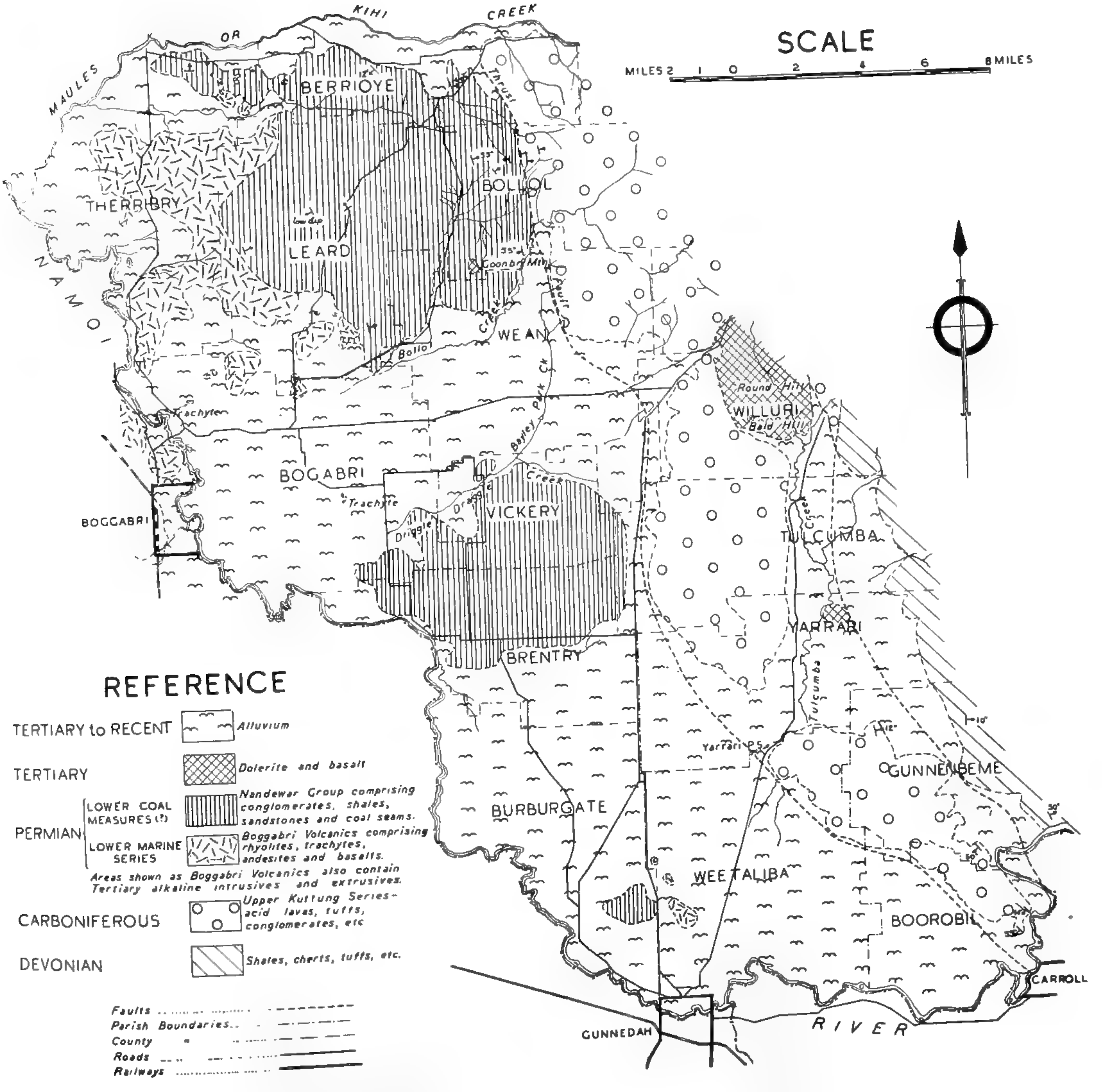
Journal Royal Society of N.S.W., Vol. LXXXII, 1948, Plate XVIII

GEOLOGICAL MAP SOUTH-WESTERN PART COUNTY NANDEWAR



by Upper Kuttung (Carboniferous) rocks, which have been overthrust from the east. The Lower Marine lavas, and in part the Lower Coal Measures, have been intruded by a group of Tertiary alkaline rocks.

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PART IV

SYNTHESIS OF DITHIOHEXESTROL DIMETHYL ETHER.

By G. K. Hughes
and E. O. P. Thompson.

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The remarkable estrogenic activity of the synthetic sex hormones stilbestrol, hexestrol and dienestrol discovered by Campbell, Dodds and Lawson (1938–9) and Dodds, Goldberg, Lawson and Robinson (1938–9) has resulted in the preparation and testing of many similar types of compounds. Investigations in these laboratories have been aimed at producing the sulphur analogues of some of these synthetic hormones and this paper reports the preparation of dithiohexestrol dimethyl ether.

The estrogenic activity of this ether is negligible ; this may be connected with the difficulty of demethylation. Hexestrol dimethyl ether was found difficult to demethylate by Dodds, Goldberg, Lawson and Robinson (1939) and the sulphur analogue is even more resistant. Hydriodic acid, pyridine hydrochloride, potassium hydroxide and the method of Schonberg and Moubasher (1944) using magnesium iodide have no effect on dithiohexestrol dimethyl ether or thioanisole. Sodium in liquid ammonia demethylates thioanisole readily but no crystalline product could be isolated in preliminary experiments with dithiohexestrol dimethyl ether. Using the same technique anisole gave a very poor yield of phenol as previously shown by Birch (1947). The stability of methyl thioether groups to disruption has also been noted by Hodgson, Sibbald and Smith (1947).

The original scheme for the synthesis of dithiostilbestrol, involved the preparation of the alcohol, 1-(*p-methylmercaptophenyl*)-*propanol*-I, by reduction of *p-methylmercaptopropiophenone*. Many attempts to isolate the alcohol from the reduction products were unsuccessful, presumably due to the great ease of dehydration to *thioanethole*, which was obtained in one of these experiments. This hydrocarbon was then used to prepare dithiohexestrol dimethyl ether, by the method of Kharasch and Kleiman (1943) in twelve per cent. yield. Only one isomer was obtained in a pure form.

EXPERIMENTAL.

Thioanisole.

Thiophenol (400 g.) was dissolved in a solution of caustic soda (160 g.) in water (2 litres) contained in a three-necked flask fitted with a stirrer. Dimethyl sulphate (510 g.) was added with stirring and cooling. When the addition was complete the mixture was refluxed for one hour and the oil separated. The aqueous layer was extracted with ether and the oil and extracts dried over calcium chloride. The solvent was removed (thioanisole is appreciably volatile in ether), and the thioanisole distilled at 192–8° C. yield 425 g. (98%).

p-Methylmercaptopropiophenone.

Finely powdered anhydrous aluminium chloride (1·1 mol.) was placed in a three-necked flask fitted with reflux condenser, stirrer and dropping funnel and cooled in ice. Carbon disulphide (400 mls.) was added and then propionyl chloride (1·2 mol.) gradually added, with stirring, to the mixture, followed by the slow addition of thioanisole (1 mol.). The viscous mixture was stirred for one hour at room temperature and finally refluxed for ten minutes. The carbon disulphide layer was then decanted and the green residue decomposed with ice and hydrochloric acid and ether extracted. The extract was washed with water and dried over calcium chloride. The solvent was removed and the ketone distilled under reduced pressure (b.p. 184° at 20 mm. approx.). The pale yellow solid (crude yield 92%) after one recrystallization from alcohol melted at 60–61° C. (82% recovery). Fractional concentration of the mother liquors gave no ortho compound. The pure ketone is a white crystalline solid, readily soluble in ether, alcohol and benzene, m.p. 61° C.

Found: C, 65·96; H, 6·54%; $C_{10}H_{12}OS$ requires C, 66·6, H, 6·6%.

The phenylhydrazone, oxime and semicarbazone of the ketone I were prepared in the usual manner, and the results are given in the table, together with the constants obtained for the sulphoxide and sulphone prepared by the methods of Gazdar and Smiles (1908) and Bost, Turner and Norton (1932).

TABLE I.

Compound	Formula.	Yield.	M.p.	Analysis.	
				Found.	Formula Requires.
Phenylhydrazone ..	$C_{16}H_{18}N_2S$	100%	83–86°	N, 10·42	10·37
Oxime	$C_{10}H_{13}ONS$		101°	N, 7·02	7·2
Semicarbazone ..	$C_{11}H_{15}ON_3S$		162°	N, 16·8	17·7
				C. H.	C. H.
Sulphoxide ..	$C_{10}H_{12}O_2S$	94%	96°	60·88 6·09	61·16 6·16
Sulphone	$C_{10}H_{12}O_3S$	58%	108°	56·25 5·67	56·55 5·7

The position of the propionyl group was indicated by alkaline cleavage of the 1-(α-methyl p-methylmercapto-phenacyl) pyridinium iodide, formed from the ketone by treatment with pyridine and iodine by the method of King, McWhirter and Rowland (1944), to the known p-methylmercapto-benzoic acid, m.p. 191° (Lit. 192°).

Preparation of Thioanethole. Reduction with Aluminium Isopropylate.

The Meerwein Pondorff Verley method of reduction described by Wilds (1944) was successful in reducing the ketone to the alcohol, though attempts to isolate the alcohol failed. However, dehydration of the crude reaction product with potassium bisulphate gave thioanethole III, in 85% yield. Unpurified aluminium isopropylate was used in these reductions and was prepared in the usual way, using 1 g. aluminium foil for each 10 g. of ketone, together with 20 ml. dry isopropyl alcohol, 0·05 g. mercuric chloride and 0·2 cc. carbon tetrachloride. An equal volume of dry isopropyl alcohol was added to the solution of aluminium isopropylate when the ketone was added. After refluxing the mixture for ten minutes the slow distillation of acetone was carried out as described by Wilds (1944). When the dinitrophenylhydrazine test of the distillate was negative, the excess isopropyl alcohol was removed under reduced pressure and the residue hydrolysed by cold dilute hydrochloric acid (2 N). The mixture was extracted with ether, washed with water, and dried over anhydrous sodium sulphate. After removal of the ether the residue was heated with as much finely divided potassium bisulphate as there was ketone, originally, for 30 minutes at 180–190° C. After cooling, the mixture was extracted with ether and removal of the solvent followed by distillation under reduced pressure gave thioanethole III, a white solid, b.p. 143° C., at 25 mm. approx. Repeated recrystallization from methanol gave a white crystalline solid, m.p. 35° C.

Found: C, 72·9; H, 7·35%. $C_{10}H_{12}S$ requires C, 73·1; H, 7·36%.

The yield of thioanethole was 85%, the product had a distinct aniseed odour and instantly decolorized bromine in carbon tetrachloride.

Note.—If the oil is distilled in a stream of nitrogen before heating with potassium bisulphate, oils are obtained which give no ester derivatives with acid chlorides and which contain small amounts only of thioanethole. Distillation under reduced pressure with an air leak increased the amount of thioanethole.

Hexestrol Dimethyl Ether.

The thioanethole (1 mol.) was converted to the hydrobromide at —80° C. and then added to phenyl magnesium bromide and anhydrous cobalt chloride at —20° C. as described by Kharasch and Kleiman (1943). After stirring for a few hours the reaction mixture was poured into ice and acidified. Separation of the organic layer was followed by extraction with benzene. The organic extracts were dried with calcium chloride and after removal of the solvents the diphenyl formed in the reaction was removed by distillation under reduced pressure. The residue distilled at higher temperatures and no separation of fractions was made (b.p. 200–300° C. at 25 mm. approx.). The weight of crude product was 11·45 g. and recrystallization from ethyl alcohol to constant melting point gave 1·9 g. (12%) dithiohexestrol dimethyl ether m.p. 153° C.

Found: C, 72·46; H, 7·90%. $C_{20}H_{26}S_2$ requires C, 72·64; H, 7·94%.

Concentration of the mother liquors gave a yellow oil which, with ether, gave a small amount of a white solid, m.p. 133–136° C. There was insufficient to identify this substance.

Demethylation of Thioanisole.

The thioanisole (0·1 mole) was suspended in liquid ammonia (250 ml.) contained in a bolt-necked flask and small pieces of sodium (0·1 mole) were added with mechanical stirring till the characteristic blue colour was permanent. Solid ammonium chloride (11 g.) was added to decompose the sodium compounds and the ammonia evaporated on the water bath. The residue was acidified, extracted with ether, the ether extract shaken with aqueous caustic soda followed by acidification and extraction of the caustic soda solution with ether. After removal of the solvent the thiophenol was distilled, b.p. 168–170°. Yield 8 g. (73%). Diphenyl disulphide was also obtained by evaporation of the ether solution after it had been extracted with caustic soda solution. This is presumably formed by oxidation of the thiophenol during its extraction.

ACKNOWLEDGEMENTS.

The authors are indebted to Miss J. Fildes for semi-microanalyses; to Mrs. A. R. Thompson, who carried out the original preparation of p-methyl mercapto-propiophenone, its oxime and semicarbazone; and to Mr. W. Whitton for testing the dithiohexestrol dimethyl ether.

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SOME EFFECTS OF COMPRESSION ON THE PHYSICAL PROPERTIES OF LOW-RANK COAL.

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INTRODUCTION.

Irreversible changes accompanying air-drying of some Australian lignites were described in a recent paper (Dulhunty, 1946). The lignites were woody homogeneous materials, believed to be the precursor of vitrain, occurring in seams of brown coal. In the fresh moist condition they were soft and dull. After removal of water by air-drying, they became hard and brittle with the fracture and lustre of vitrain in sub-bituminous coal. The changes were found to be permanent as the lignites did not return to the soft dull condition when re-saturated with water. It was concluded that the lignites had reached a critical stage in rank advancement where the micelles were just touching with very small contact areas, and that the removal of water by air-drying allowed surface attraction to deform the micelles, reducing intervening spaces, and increasing contact areas and cohesive forces. This change in structure was believed to be responsible for development of hardness and bright lustre, and to account for the irreversible nature of the physical changes on the assumption that the internal pressure of adsorbed water, on re-saturating, was insufficient to overcome the increased cohesive forces.

Results recorded in this paper provide experimental evidence which supports the foregoing theory, and throw some light on the mechanism of physical rank advancement during natural metamorphism of coal.

NATURE OF PROBLEM AND OBJECTS OF EXPERIMENTS.

The changes described above were observed in lignites from Kiandra and Berridale in New South Wales, and from Yallourn in Victoria. More recent observations in Australia, Europe and America suggest that all brown coal seams pass through a critical stage in rank advancement during which the woody components, destined to become vitrain, exhibit permanent changes in hardness and lustre on air-drying. This may be described as the *high-rank brown-coal* stage at which the woody material is almost black, but soft and dull, with a maximum inherent moisture content of 65 to 80% (dry coal basis), a carbon content of 65% to 70% and a volatile yield of 40% to 50% (ash-free dry basis). It is regarded as a critical stage in rank advancement as the material appears to be ready to change to hard bright vitrain if natural metamorphism continues. This transformation, which takes place under water-saturated conditions in the earth's crust, is accompanied by reduction in maximum inherent moisture from the vicinity of 75% to about 25%. The changes are permanent as vitrain of sub-bituminous coal does not return to the soft dull condition when overlying strata are removed by mining operations or erosion.

The physical changes accompanying air-drying of woody lignite are similar in character to those which take place as a result of natural metamorphism or rank advancement, and it appears probable that modification of micelle structure may be similar in each case. If this is so, the changes in structure on air-drying would be due to operation of attractive forces between the micelles when water is removed by evaporation, and in the case of natural metamorphism it would take place when pressure from overlying strata together with the forces of surface attraction exceed the internal pressure of adsorbed water. In view of this it appeared that it might be possible to induce permanent physical changes in hardness, moisture and lustre of lignite, without air-drying, as in the process of natural metamorphism, by application of an external compressional force which, added to the attractive forces between the micelles, exceeded the internal pressure of water adsorbed in inter-micelle spaces, if time of application was sufficient to allow deformation of the micelles and expulsion of water. With this object in view experiments were designed to reproduce, in the laboratory, conditions of temperature and compression, under water, similar to those in natural metamorphism, in an attempt to bring about permanent physical changes or advancement of physical rank.

APPARATUS AND EXPERIMENTAL TECHNIQUE.

Apparatus consisted of a press (illustrated in figure 1) designed to compress lignite and maintain compression during contraction of the material while immersed in a water bath at temperatures up to 100° C., or enclosed in a pressure vessel at higher temperatures. The pressure vessel was that described in an earlier publication (Dulhunty, 1942).

The press was provided with a heavy spiral spring arranged so that its force, when screwed down, operated against plungers at both ends of a pressure cylinder containing lignite. The spring was of sufficient length to maintain at least 95% of its original force, during contraction of the lignite, between stages at which it was reset. In experimental work the spring was used to provide a force of one ton at about two-thirds full compression. Three pressure cylinders with diameters of $\frac{3}{4}$, $\frac{1}{2}$ and $\frac{3}{8}$ in. were used for the purpose of obtaining compressional forces of approximately 5,000, 11,000 and 22,000 lb. per sq. in. respectively from the spring pressure of one ton. According to calculations previously recorded (Dulhunty, 1944) these compressional forces would be equivalent to about 4,300, 9,500 and 19,000 feet of coal-measure strata respectively.

Lignite used for charging the pressure cylinders was in the form of rods cut at right angles to the bedding plane. This orientation was adopted so that compressional force would be applied in a direction similar to that in which weight of overlying strata had acted in the past, and would continue to act on the seam during subsequent metamorphism if coalification continued.

In each experiment the rod, cut from lignite in its original water-saturated condition, was turned down until it would just slide into the pressure cylinder, care being taken to keep the material wet. The cylinder was then immersed in water to exclude air ; the lignite was inserted ; and the two plungers were placed against the ends of the rod, which was moved to a central position in the cylinder. The portions of the plungers protruding at each end of the cylinder were measured accurately to obtain the length of the rod. The cylinder was then placed in the press ; the spring was screwed down ; and the press, charged with lignite under compression, was immersed in oxygen-free water and heated at the required temperature. At various intervals (see Table 3) the press was cooled down and removed from the water to measure contraction of the lignite, reset the spring, or remove test pieces of lignite for examination.

GENERAL EFFECTS OF COMPRESSION UNDER WATER.

Preliminary tests were carried out on woody lignite (from Berridale, N.S.W.), pieces of which became bright and hard on air-drying. A rod cut from the soft dull material in its original water-saturated condition was pressed in a ½ in. cylinder, under water, at 27° C. with a compressional force of 11,000 lb. per sq. in. for a period of seven days. After compression the lignite was somewhat harder and fresh fracture surfaces exhibited a faint silky sheen, but on soaking in water for 24 hours it returned to the original soft dull condition. The test was then repeated at a temperature of 100° C. When removed from the press the lignite was hard and brittle and exhibited a bright lustre when fractured, and it did not return to the soft dull condition when soaked in water for six months. As far as could be judged by observation, the hardness and lustre were identical with those produced by air-drying, and the material could not be distinguished from the vitrain of sub-bituminous coal. Furthermore it did not crack, or break up when air-dried. No change in chemical properties, as a result of heating at 100° C. for seven days, could be detected by proximate and ultimate analyses carried out on the pressed material and control samples. During compression maximum inherent moisture was reduced from 76% to 24% and no increase took place after soaking in water for six months.

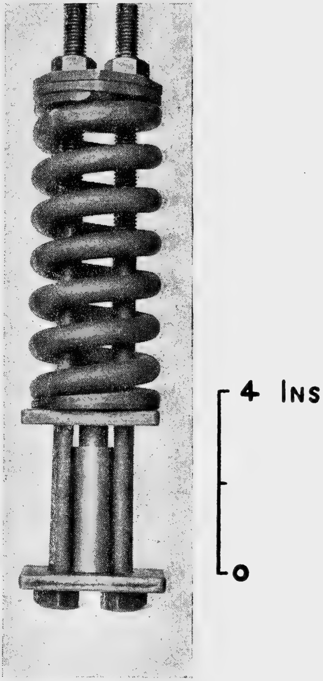

Fig. 1.

This experiment demonstrated the fact that irreversible changes in hardness, lustre and moisture content could be produced in lignite by application of compressional force under water at temperatures, which although slightly elevated were too low to cause thermal decomposition over the period of heating.

A number of tests, employing conditions similar to those described above, was carried out on other pieces of woody lignite from Berridale, as well as pieces from Kiandra, Yallourn and Moorlands. Permanent physical changes were produced in all cases, but it was found, in general, that two kinds of lustre and structure were developed in different pieces of lignite from the same occurrence. Some pieces developed bright·resinous lustre and conchoidal fracture very similar to vitrain. Others assumed a silky sheen and fibrous structure somewhat resembling fusain. Close examination of the original materials revealed slight differences. Those which produced material resembling vitrain after compression were a little more homogeneous and less fibrous than those which gave rise to material like fusain. The differences, however, were ill defined and both were soft and dull with the typical macroscopic grain-structure of wood, but after compression the two kinds of lustre and structure were quite distinct. The production of material resembling vitrain could be obtained by air-drying, but the fusain structure could not be produced as satisfactorily as by compression.

The foregoing observations suggest that differentiation of wood into the precursors of vitrain and fusain had taken place in the lignite at advanced brown-coal rank, although there was very little difference in superficial appearance. Application of compressional force to these materials appears to induce physical changes similar to the natural transformation of lignite to sub-bituminous coal, at which stage vitrain and fusain assume their separate physical identities. It also appears as though physical rank can be advanced to some extent without change in chemical rank, as no changes in proximate and ultimate composition took place during compression in the laboratory tests.

In experiments already referred to, and in those to be described later, removal of lignite rods from the cylinders was facilitated by an interesting phenomenon which followed release of spring pressure. Under pressure the lignite rod is pressed hard against the wall of the cylinder. Immediately after release of pressure the diameter of the rod decreases, and its length increases sufficiently to allow it to slide freely up and down the cylinder. After about 20 minutes, however, the diameter commences to increase again and the length decreases, with the result that the rod becomes tight in the cylinder and considerable force is necessary to move it from one position to another. Removal of rods could be effected with ease during the interval of 20 minutes following release of spring pressure. The dimensions of the changes were very small, probably less than 0·5%, but they were sufficient first to allow the rod to slide freely, and then to cause it to become tightly held in the cylinder.

Relative Influence of Time, Temperature and Pressure.

Additional experiments were carried out to obtain qualitative evidence of the relative influence of time, temperature and pressure in the development of permanent physical changes.

A large piece of Berridale lignite, possessing the properties summarized in Table 1, was selected for the experiments. It was soft, dull, and relatively homogeneous, although the original grain-structure of the wood was evident, and the material showed a distinct tendency to split along the grain as in normal wood. When dried in air it became hard and bright, and the fracture (essentially conchoidal) showed very little relation to the original grain-structure, or to the bedding plane of the seam in which it was embedded.

Six experiments were carried out under different conditions of time, temperature and pressure, as indicated in Table 2. At various intervals during each experiment contraction of the lignite was measured and a small test piece

TABLE I.

Properties of Berridale Lignite.

Maximum inherent moisture (dry basis)	79·52%
Proximate analysis (A.F.D. basis)—	
Volatiles	53·17
Fixed carbon	46·83
Ash (dry basis)	1·49
Ultimate analysis (A.F.D. basis)—	
Carbon	69·05
Hydrogen	5·29
Oxygen, nitrogen and sulphur	25·66

Geological age : Tertiary.

For nature of occurrence, see Dulhunty (1946).

was removed from the press to determine the extent to which permanent changes had developed. This was done by moving the lignite rod until the required amount protruded from the cylinder, and then cutting off the protruding portion so that the remaining section of the rod presented a flat face to the plunger when the press was reassembled. Immediately after removal from the press, each test piece was fractured to examine hardness and lustre. The broken pieces were then placed in water for four days to test the permanency of the physical changes. A period of four days was found to be sufficient to allow the lignite to reach stability. Some pieces were allowed to remain in water for as long as six months, but no further changes were detected. After soaking in water for four days, the pieces were again fractured to detect any reduction in lustre and hardness, and then maximum inherent moisture was determined.

Results of the experiments are summarized in Table 3. In experiment 1 the changes were complete and permanent, with a reduction in maximum inherent moisture to 24·8%, and it is evident that the conditions of time, temperature and pressure were greater than necessary to effect the changes. In experiment 2 the changes were almost complete at stage 1 with reduction in moisture to 37·4%, and complete at stage 2, where moisture reached 23·2%. Experiment 3 demonstrates the gradual development of physical changes and reduction of moisture to 24·7% at stage 4, where the changes became permanent. In experiment 4, the conditions were such that the changes were still incomplete at stage 5, after 153 days, when moisture had been reduced to 45·8% and the rate of change in physical properties had become extremely slow. The changes proceeded further in experiments 5 and 6, and moisture was reduced to about 36%, but the time in each case was insufficient to effect complete and permanent changes.

TABLE 2.

Experimental Conditions.

Experiment.	Diameter of Cylinder. (Inches.)	Compressional Force. (Lb. per sq. in.)	Temperature. (° C.)	Time. (Days.)	Gas Pressure on Water. (Ats.)
1	$\frac{3}{4}$	5,000	125	7	10
2	$\frac{3}{4}$	5,000	100	16	5
3	$\frac{3}{4}$	5,000	70	48	3
4	$\frac{3}{4}$	5,000	25	153	1
5	$\frac{1}{2}$	11,000	25	139	1
6	$\frac{3}{8}$	22,000	25	87	1

TABLE 3.

Results of Compression of Lignite.

Exp. No.	Stage No.	Time. (Days.)	Contraction. (% Orig. Vol.)	Max. Inh. Moist.	Properties after Compression.		Effect of Standing in Water for Four Days.
					Lustre.	Hardness.	
1	1	7	37·1	24·8	Very bright.	Hard, brittle.	No change.
2	1	1	32·29	37·4	Bright.	Hard.	Slight reduction in lustre and hardness.
	2	4	37·3	23·2	Very bright.	Hard, brittle.	No change.
	3	16	40·65	20·9	Very bright.	Hard, brittle.	No change.
3	1	2	32·1	51·8	Medium, bright.	Medium, hard.	Returned to soft dull condition.
	2	6	34·26	45·8	Bright.	Hard.	Returned to medium bright and medium hard.
	3	20	36·59	35·0	Bright.	Hard, medium brittle.	Slight reduction in lustre and hardness.
	4	48	38·03	24·7	Very bright.	Hard, brittle.	No change.
4	1	2	24·15	57·8	Dull.	Soft.	Remained dull and soft.
	2	6	30·57	52·2	Dull.	Soft.	Remained dull and soft.
	3	23	33·45	50·2	Faint bright.	Medium hard.	Returned to dull soft condition.
	4	51	35·45	48·7	Medium bright.	Medium hard.	Returned to dull soft condition.
	5	153	37·95	45·8	Bright.	Hard.	Returned to medium bright and medium hard
5	1	19	32·3	55·0	Bright.	Hard.	Returned almost to original condition.
	2	52	36·98	42·6	Bright.	Hard.	Returned to medium bright and medium hard.
	3	139	41·66	36·9	Very bright.	Hard.	Slight reduction in lustre and hardness.
6	1	2	26·35	48·0	Dull.	Soft.	Remained dull and soft.
	2	17	34·7	40·0	Medium bright.	Medium hard.	Returned almost to original condition.
	3	51	41·45	37·2	Bright.	Hard.	Returned to medium bright and medium hard.
	4	87	44·95	36·4	Very bright.	Hard, brittle.	Slight reduction in lustre and hardness.

The following conclusions may be drawn from the results :

(1) Both rate and extent of change in physical properties are functions of time, temperature and compressional force, and each factor operates as an independent variable.

(2) Under any given conditions of temperature and compressional force, rate of change becomes progressively slower with increasing time.

(3) Under certain conditions of temperature and compressional force (as in experiment 4) the rate of change may become infinitely slow before complete and permanent changes are effected, but with infinite time, which in relation to laboratory conditions is equivalent to geological time, the changes would eventually take place.

(4) With rise in temperature, the rate of change in physical properties increases very rapidly. This is evident from results of experiments 2, 3 and 4, in which a given compressional force of 5,000 lb. per sq. in. produced permanent changes in four days at 100° C., and in 48 days at 70° C., while at 25° C. it appeared that almost infinite time would be required. Similarly, the force of 5,000 lb. reduced moisture from 80% to 45% in less than one day at 100° C., in six days at 70° C., and in 153 days at 25° C.

(5) With increase in compressional force, the rate of change in physical properties increases rapidly. This can be seen from results of experiments 4, 5 and 6 (carried out at 25° C.) in which moisture was reduced to the vicinity of 45% in 153 days at 5,000 lb., in about 40 days at 11,000 lb., and in about three days at 22,000 lb.

(6) Under any conditions of temperature and compressional force, irreversible changes to the bright hard condition take place when moisture content is reduced to about 24%, and the volume of the material is reduced to about 40% of that which it occupied in the *high-rank brown-coal* stage.

(7) Progressive changes in lustre and hardness are reversible (on release of spring-pressure) until a critical stage is reached, after which they become irreversible. This is believed to be the stage at which the inter-micelle contact areas become sufficiently large to provide cohesive forces greater than the internal pressure of adsorbed water.

(8) Naturally occurring vitrain, in sub-bituminous coal, is permanently bright, hard and brittle, and it has a maximum inherent moisture content in the vicinity of 25%. As similar " vitrain ", with comparable moisture content, was produced by compression of lignite, under water, at temperatures and pressures within limits normally expected at relatively shallow depths in the earth's crust, it is believed that the actual mechanism of natural metamorphism was reproduced in the laboratory and demonstrated by the results of experimental work.

Results recorded in this paper are essentially qualitative and of a preliminary nature. Improved apparatus and technique are at present being designed with the object of obtaining exact quantitative data regarding relations between time, temperature and pressure, and rate of change in physical properties, during the physical metamorphism of coal.

ACKNOWLEDGEMENTS.

In conclusion it is wished to acknowledge facilities provided from the Commonwealth Research Grant to the University of Sydney ; valuable discussion with Dr. D. H. Bangham, B.C.U.R.A., London, and Dr. T. Iredale, Department of Chemistry, University of Sydney ; and also the assistance of Miss N. Hinder in laboratory work.

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MINERALOGICAL EXAMINATION OF SOILS DEVELOPED ON THE PROSPECT HILL INTRUSION, NEW SOUTH WALES.*

By Roy Brewer, B.Sc.
(Communicated by Dorothy Carroll.)

Manuscript received, November 10, 1948. Read, December 1, 1948.

CONTENTS.

INTRODUCTION.

A soil survey of an area of 114 acres at Prospect Hill, N.S.W., was carried out in 1947 following its acquisition (Brewer, 1947) as the site for the new Sheep Biology Laboratory under the control of the Division of Animal Health and Production, C.S.I.R. It is situated 19 miles from Sydney on the Great Western Highway, and comprises two adjoining blocks, Portions 27 (part), 31, 32, 33, Parish of Prospect.

It was decided during the soil survey to attempt an investigation of the contamination of one soil parent material by another situated higher up the slope, by means of mineralogical analyses, and also to determine the usefulness of soil mineralogy as an aid in fixing soil boundaries where they are not obvious on the surface. Investigations were confined to the larger paddock surveyed (Fig. 1), which is situated on the eastern edge of the Prospect Hill intrusion and so affords the opportunity of studying the contaminating effects of a basic igneous rock situated on a rather steep hill above an area of Triassic sediments.

GEOLOGY AND TOPOGRAPHY.

The main topographic feature of the area is a moderately steep hill situated in the south-west corner and rising to a height of approximately 360 feet above sea-level. From this hill the country falls away rather sharply, the slope becoming progressively more gentle away from the hill down to the creek-lines around the base of the slopes at about 180 feet above sea-level. One of these creeks flows from west to east and is large enough to have built up narrow alluvial flats within the area being studied.

The chilled margin of the Prospect Hill intrusion forms the bed rock of the upper slopes of the hill. This intrusion is described (Jones *et al.*, 1911) as an

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MINERALOGI

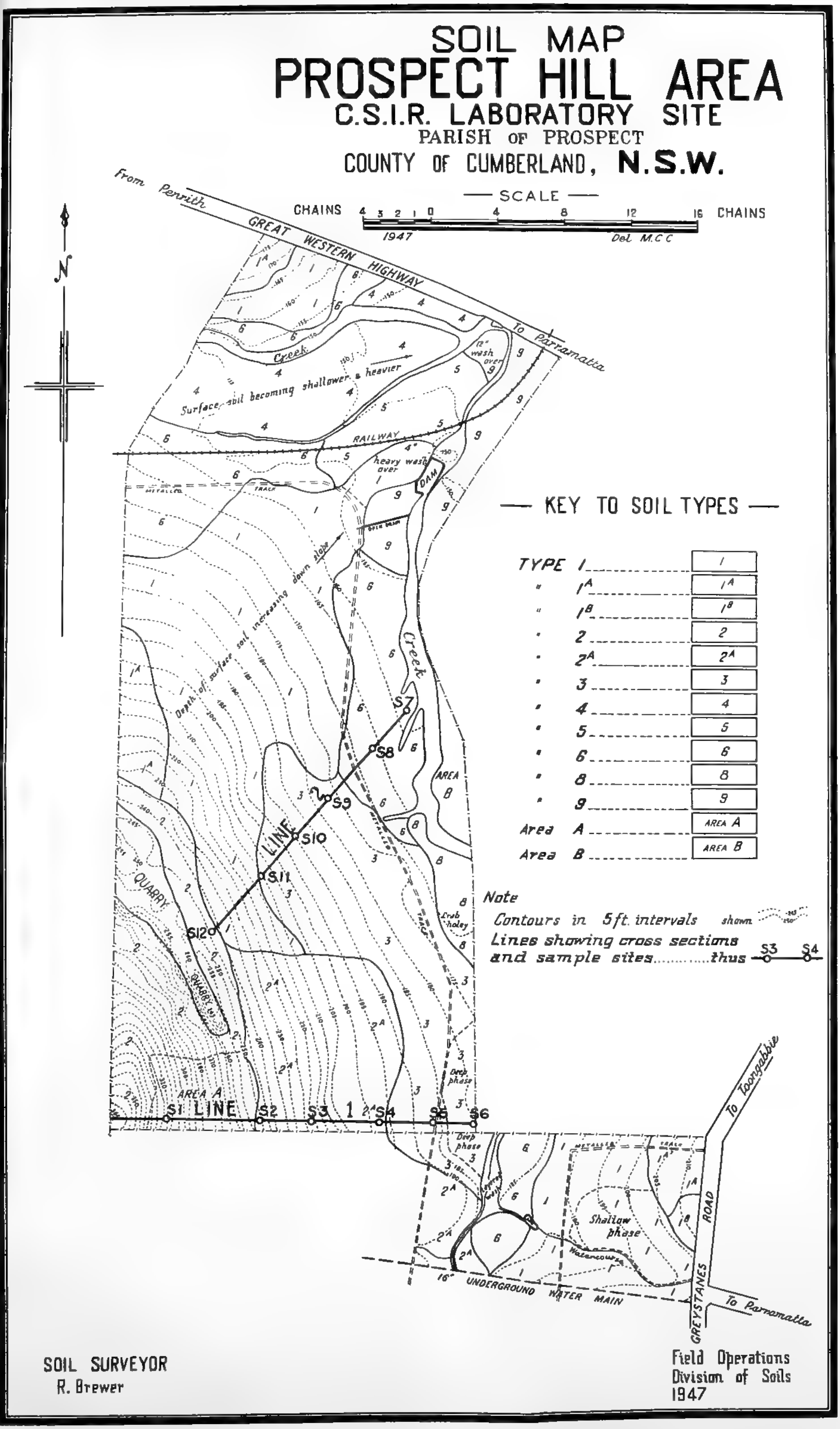
SOIL MAP
PROSPECT HILL AREA
C.S.I.R. LABORATORY SITE
PARISH OF PROSPECT
COUNTY OF CUMBERLAND, N.S.W.
— SCALE —
CHAINS 4 3 2 1 0 4 8 12 16 CHAINS
1947
Del. M.C.C.
N
From Penrith
GREAT WESTERN HIGHWAY
To Parramatta
Creek
Surface soil becoming shallower & heavier
12" wash over
RAILWAY
heavy wash over
DAM
METALLED
TRACK
Depth of surface soil increasing down slope
Creek
AREA B
LINE
S7
S8
S9
S10
S11
S12
QUARRY
QUARRY
AREA A
S1 LINE
S2
S3
S4
S5
S6
Deep phase
Crab holey
Deep phase
Shallow phase
Watercourse
16" UNDERGROUND WATER MAIN
GREYSTANES ROAD
To Toongabbie
To Parramatta
— KEY TO SOIL TYPES —
TYPE 1 — 1
" 1A — 1A
" 1B — 1B
" 2 — 2
" 2A — 2A
" 3 — 3
" 4 — 4
" 5 — 5
" 6 — 6
" 8 — 8
" 9 — 9
Area A — AREA A
Area B — AREA B
Note
Contours in 5ft. intervals shown
Lines showing cross sections and sample sites thus S3 S4
SOIL SURVEYOR
R. Brewer
Field Operations
Division of Soils
1947

Fig. 1.

essexite, the chilled margin of which resembles a basalt very closely in the hand specimen. The bed rock of the surrounding country is Triassic sediments into which the essexite has been intruded. These sediments consist of the Hawkesbury Series and the Wianamatta shale but, as there are no outcrops on the area it was not possible to determine which of these series forms the country rock. It is considered that the junction between the intruded rock and the surrounding Triassic sediments is quite steep and sharp (Jones *et al.*, 1911).

THE SOILS.

Detailed descriptions of the individual soil types can be obtained from the report on the soil survey (Brewer, 1947). In general the property consists of an area of Black Earths formed on the basaltic material of the chilled margin of the intrusion with podsolised types formed on the Triassic series on the lower slopes. A small area situated geographically between these two major soil groups was suspected as being of the Black Earth type over a substratum of light coloured clay formed on the Triassic series.

The true Black Earths consist of very dark brown to black, well-structured clays sometimes over browner clays which contain an accumulation of calcium carbonate in the form of concretions and sometimes (on top of the basaltic hill where the soils are rather shallow) directly over decomposed basaltic material into which they pass gradually. The podsolised types consist of greyish brown to brownish grey loams, silt loams, and silty clays, with some development of a bleached A_2 horizon, over variously coloured mottled clays sometimes with small accumulations of calcium carbonate in the B_2 horizon. The soils of the area between the Black Earths and the podsolised soils consist of dark coloured clay or silty clay over a browner clay containing some accumulations of calcium carbonate. This again overlies a light grey coloured clay which is not unlike some of the clays found under true Black Earths where they are residual soils. This clay is identical in appearance with the light coloured clays found under the podsolised soils where they were bored to sufficient depth.

In the survey of the unit discussed in this paper there is a complicated pattern of eight soil types, with three additional varieties or phases of those types (see Fig. 1). Of these soil types, T_2 and T_2A are of direct basaltic origin, and the remainder related to Triassic sediments as parent material.

SAMPLING.

Samples for mineralogical analyses were taken at varying intervals along two lines (see Fig. 1) from the top of the hill to the creek line at the bottom of the slope. Line I followed the southern boundary fence of the area, and the samples were taken at the following distances from the crest of the hill:

S_1, 225 feet; S_2, 580 feet; S_3, 780 feet; S_4, 1050 feet; S_5, 1260 feet; S_6, 1450 feet.

In all cases the surface soil (0–6 inches) was taken and from S_2 onwards the subsoil was sampled from 24 to 30 inches. S_2 was sampled at a depth of 4 feet, at which depth the type of clay changed suddenly. S_1 was not sampled except for the surface soil because there appeared to be no significant change in the profile until the decomposed basaltic material was reached. The samples were taken with a hand auger, care being taken to prevent contamination of the samples, particularly in the sampling of the subsoils.

A similar procedure was followed for Line II, sampling from the creek line at the bottom of the slope up the slope to a small open quarry in the basaltic material. The intervals of sampling were:

S_7, 0 feet; S_8, 200 feet; S_9, 460 feet; S_{10}, 660 feet; S_{11}, 895 feet; S_{12}, 1145 feet.

In this case surface (0–6 inches) and subsoils (24–30 inches) were sampled at all sites.

For completeness and comparison the following miscellaneous samples were taken and examined:

S_{13}: A sample of Triassic sandstone probably belonging to the Ostracod Beds, since it was calcareous. This outcropped on the Great Western Highway just outside the area.

S_{14}: A sample of soil developed on shale occurring at the same location as S_{13}.

S_{15}: A sample of the B_1 horizon of the black alluvial soil formed on the alluvial flats of the creek at the foot of the hill slope.

S_{16}: The sample of the deep subsoil at 4 feet taken at site S_2 on Line I.

PREPARATION OF CONCENTRATES.

Investigations were confined to the fraction from 0·4 mm. to 0·02 mm., which includes the fine sand fraction and the finer end of the coarse sand fraction.

100 gm. lots of the air-dried samples were used for the concentration and separation of the heavy minerals. The soils were dispersed by means of an electric mixer with the aid of " calgon " as a dispersing agent. Twenty minutes' mixing was found to be sufficient for complete dispersion. Partial separation of the clay and silt was then obtained by the sedimentation process, which was carried out in 600 ml. beakers allowing the appropriate time for settling through 10 cm. at the prevailing temperature. The samples were then washed through a 0·4 mm. sieve with a stream of water from a wash-bottle. It was found that very little, if any, of the sample was held on the sieve, and this was discarded. Surface soils were then treated with 100 ml. of 10% hydrogen peroxide to remove organic matter. The separation of the fine sand fraction by sedimentation was then carried to its conclusion. All samples were then given successive treatments with 100 ml. of twice normal hydrochloric acid on a sand-bath at approximately 100° C. for 2 hours, until the liquid at the end of the treatment was almost colourless. This acid treatment removed iron oxide coatings from the grains. The acid was removed after each treatment and at the end of the treatments by washing with water, allowing to stand as for the sedimentation process, and decanting the supernatant liquid. The samples were then dried on the sand-bath and the fine sand was weighed.

10 gm. lots of the fine sand fractions were weighed out for separation by the heavy liquid method, bromoform of specific gravity $2{\cdot}83 \pm 0{\cdot}01$ being used. The separation was carried out in evaporating dishes.

The percentage of heavy minerals in the soil was calculated from the weight of heavy minerals recovered from 10 gm. of fine sand, the weight of total fine sand, and the weight of soil used for the separation. This almost certainly gives a low value, as the coarse silt and perhaps the coarser sand would contain some heavy residues. However, it is thought that, although these percentages are not strictly accurate, they can be compared one with another, since the same size-fraction has been used in all cases for the concentration of the heavy minerals.

The sandstone from the Triassic series was soft, calcareous and partially weathered, and complete disaggregation was obtained by careful crushing in an agate mortar. 100 gm. of this sample was then treated in the same way as the soil samples.

MICROSCOPIC EXAMINATION.

For purposes of identification of the mineral grains a small portion of the heavy concentrates was separated into strongly magnetic, magnetic and non-magnetic fractions by means of a bar magnet and a strong electromagnet. These fractions were then separately mounted on gelatinised microslides following the method outlined by Marshall (1945). Where this separation was deemed unnecessary a single mount of the sample of the total heavy concentrate was made on the gelatinised microslides. Identifications were then made by the usual optical observations, and with the aid of a very limited range of refractive index liquids. For the optical observations clove oil (RI ÷ 1·54) was used on the gelatinised microslides as the immersion medium. A stream of acetone from a wash-bottle was used to remove the refractive index liquids after the determinations were made, and it was found that satisfactory permanent mounts could then be prepared by adding a small amount of Canada balsam to the gelatinised mounts, cooking for the requisite time, and then covering carefully with a coverslip.

Soils from sites S_1, S_{13}, S_{14}, S_{15} and S_{16} were examined in detail. It was considered that S_{13} (the Triassic sandstone), S_{14} (the soil developed on shale), and S_1 (the surface soil of the Black Earth developed near the top of the basaltic rise) would represent the possible parent materials of the soils, i.e. the mineralogical assemblages would be close to those of the weathered sandstone, shale and basaltic material respectively. Since there were no outcrops of the Triassic series on the area, both the sandstone and the shale were considered.

The mineralogical analyses of these samples are given in Table 1. The remaining samples are not described in detail, but contain mixtures of varying proportions of the heavy minerals found in S_1, S_{13} and S_{14} soil samples.

TABLE 1.

	Magnetite and Ilmenite.	Leucoxene.	Zircon.	Tourmaline.	Pyroxene (*a*).	Pyroxene (*b*).	Hornblende.	Rutile.	Garnet.	Monazite.	Anatase.	Riebeckite.	Pleonaste.	Picotite.	% Heavy Concentrate in the Soil.
S_1..	A	R	VR		VA		+	+							12·9
S_{13}		F	O	C				R	+			?	?	?	0·06
S_{14}	R	VA	O	C		R		R		+					0·12
S_{15}	F	C	R	VR	R	VR		+		+	+	?			2·7
S_{16}	C	F	R	R			+	VR							0·11

F = flood = > 70% of heavy concentrate.
VA = very abundant = 50–70%.
A = abundant = 30–50%.
C = common = 10–30%.
O = occasional = 5–10%.
R = rare = 1–5%.
VR = very rare = 0·1–1%.
+ = < 0·1%.
? = doubtful identification.

DESCRIPTION AND DISTRIBUTION OF THE HEAVY MINERALS.

(1) *Zircon.* Is present as euhedral crystals, and worn and rounded grains. The shape of the crystals varies from short and stumpy, with terminal faces well developed, to tabular and, rarely, almost acicular with and without terminal faces. Inclusions are common and usually submicroscopic but sometimes larger and rod or tabular shaped, arranged parallel to the length of crystals. The mineral is colourless, but numerous minute inclusions sometimes give a cloudy grey appearance to the grains. Zoning was noted in some grains. The grains are dominantly at the lower end of the size fraction used. No particular concentration of any of the several varieties was noted in any one sample, all varieties seemingly occurring in all the samples examined.

(2) *Tourmaline.* Occurs in prismatic crystals rarely with poorly developed terminal faces, rounded worn grains and irregular grains. The colour and

pleochroism are very variable, grains occurring in varying shades of blues, browns, slate grey, buff and, rarely, green. Irregular colour zoning, especially in blues and browns, is fairly common, and this zoning occurs largely in the irregularly shaped grains. The grain-size is very variable. Again no particular occurrence of any of the several varieties is apparent, but tourmaline is absent from the basaltic material.

(3) *Rutile.* Is present in deep brown to yellow grains, often with good prismatic habit and sometimes rounded, irregular, or the typical bean-shape of worn grains. It shows the typical high adamantine lustre and appears to be largely primary, although compound grains of rutile and ilmenite were noted. Several of these compound grains appear to be a result of alteration of rutile to ilmenite rather than ilmenite to rutile. This is indicated by the fact that the ilmenite forms the borders and patches and fine streaks parallel to the length of the crystals, which are largely rutile and appear by their shape to belong to the tetragonal system. The grain-size is very variable. Rutile has a wide distribution, being present in all samples.

(4) *Pyroxene.* (*a*) The pyroxene of the basaltic material occurs in large irregular to subhedral prismatic crystals. It is purplish brown to neutral in colour and somewhat cloudy, with cleavage traces, very slight pleochroism and a large extinction angle, $Z \wedge c = 44^\circ$.

(*b*) The pyroxene of the sedimentary rocks occurs in clear, purplish grains with cleavage traces poorly developed. The grainsize is rather small. Pleochroism is very faint and the extinction angle is large. The grains are usually irregular in shape.

(5) *Leucoxene.* Is present in irregular and rounded grains as an alteration product after ilmenite. It occurs in varying amounts in all the samples examined. The grain-size is variable, but generally slightly towards the upper end of the size-fraction used.

(6) *Ilmenite.* Occurs in irregular grains of size about the middle of the size-fraction used. It is opaque, with a bluish grey lustre in reflected light, and generally shows alterations to leucoxene. It is present in most of the samples examined.

(7) *Magnetite.* Occurs very similarly to ilmenite, from which it is difficult to distinguish. It is silver grey in reflected light.

(8) *Garnet.* Occurs very rarely in the sample of Triassic sandstone. The grains are irregular and colourless with the typical rough surface. The grain-size is slightly towards the upper end of the size fraction used.

(9) *Hornblende.* Is present in the basaltic soil and in the deep subsoil at site S_2, viz. (S_{16}). Its occurrence is very rare, there being only a few grains in each sample. It is green to brownish green in colour. The grain-size is about the middle of the size-fraction used.

(10) *Monazite.* Occurs in several samples as one or two rounded yellowish grains with the typical rough surface and high birefringence and relief. It was identified in the sample of soil on the shale (S_{14}) and the alluvial soil (S_{15}).

(11) *Riebeckite.* Occurs as irregular grains in the sample of Triassic sandstone (S_{13}) and the alluvial soil (S_{15}). It is in small, elongated, slightly fibrous grains, deep blue in colour and rather strongly pleochroic with a small extinction angle. It is very rare in occurrence.

(12) *Pleonaste.* Occurs as a single doubtful grain in the sample of Triassic sandstone (S_{13}). The grain is small, green and isotropic with high relief.

(13) *Picotite.* Has a similar occurrence to pleonaste. The grain is almost opaque, with brown translucent edges.

(14) *Anatase.* Is present as a few euhedral, square crystals of anthigenic origin in the sample of the alluvial soil (S_{15}). The grain-size is very small.

DETERMINATION OF SOIL BOUNDARIES.

A study of the heavy concentrates of the samples of Triassic sandstone (S_{13}), the soil developed on shale (S_{14}), and the basaltic material (S_1) showed a close similarity between the mineral assemblages of the sandstone and shale soils and a wide dissimilarity between these and the mineral assemblage of the basaltic material. The abundance of pyroxene in the basaltic assemblage and the significant zircon and tourmaline in the shale soils and the sandstone indicated that these three minerals could be used, together with the percentages of total heavy concentrates, to determine the origin of and the admixing of the parent materials of the area. Of these, the pyroxene, zircon and percentage of total heavy concentrate gave significant results in the attempt to determine soil boundaries by changes in mineral assemblages. Approximately quantitative estimates of these three units were obtained by the method of separation of the heavy concentrates and then by a count of about 1000 grains in each sample. These estimates were made on all the samples collected (both surfaces and subsoils) on Line 1 and Line 2 and are plotted as histograms (Figs. 2, 3). The profile of the land form has been drawn on each graph by plotting height above sea-level in feet against distance in feet from the south-west corner of the area for Line 1 and from site S_7 near the creek line for Line 2. The positions of the sampling sites have been marked on these profiles (Fig. 1).

Figure 2 deals with the surface soils and subsoils on Line 1 and shows, plotted against distance in feet from the south-west corner of the area (i.e. for the position of each sampling site) the percentage of pyroxene in the soil, the percentage of zircon in the soil and the ratios of $\frac{\text{percentage of pyroxene}}{\text{percentage of total heavy concentrate}}$ in the soil, and $\frac{\text{percentage of zircon}}{\text{percentage of total heavy concentrate}}$ in the soil. The percentage of heavy concentrate in the soil is also shown separately. The ratios were plotted to show that the percentage of total heavy concentrate in the soil was not the only significant factor.

Figure 3 deals with the surface soils and subsoils on Line 2. The profile of the landform and the percentage of total heavy concentrate and the percentage of zircon in the soil have been plotted for both the surface soils and the subsoils. The percentage of pyroxene in the soil has also been plotted for the surface soils.

DISCUSSION.

A study of the histograms shows several sharp breaks in the mineralogical constitution of the soils, and these breaks correspond to soil boundaries.

The histograms for the surface soils of Line 1 show a major break in parent material occurring between S_3 and S_4 and probably centred about a point 1000 feet from the south-west corner of the area. This break is shown on the histogram by a sudden fall in the percentage of pyroxene followed by a flattening off, by a sudden rise in the percentage of zircon, by a very sudden fall in the ratio of percentage of pyroxene to percentage of heavy concentrate and by a very sudden rise in the ratio of percentage of zircon to percentage of heavy concentrate. The total heavy concentrate histograms also show a sharp fall to a point beyond S_3 with a gradual fall from that point to the foot of the hill slope.

The histograms for the subsoil sample of Line 1 show practically no change in the amount of zircon over the whole line except for an increase between S_2 and S_3 coming down the line. On the other hand the pyroxene shows a steady but very slight increase from the lower slopes up to the subsoil at S_2, where it rises very sharply. At S_1 the boring went straight on to decomposed basalt, so the subsoil has been taken as having the same mineral assemblage as the surface soil. Thus between S_2 and S_3 there is a sudden change in the parentage of the subsoil material.

From this it can be deduced that the subsoils of the podsolised soils have a fairly uniform parentage which continues under S_3 and which is intermediate in type between material derived from the basaltic chilled margin of the intrusion and the Triassic series. The percentage of total heavy concentrate in these subsoils also indicates uniform parentage.

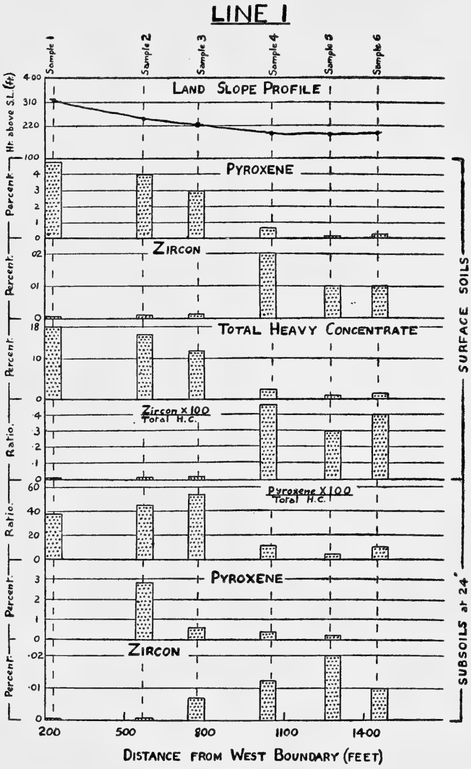

Fig. 2.

From this discussion it can be said that there is evidence of two breaks in the origin of the parent materials of the soils based on the mineralogy of the surface soils and the subsoils of the profiles. These supply evidence of the existence of soil boundaries at the points where the changes occur, namely between S_2 and S_3 and between S_3 and S_4. The first break is in the subsoil and indicates the presence of a double profile and the soil boundary between T_2 (Area A) and

T_2A (Fig. 1). The second break shows in the surface soils and indicates the existence of the soil boundary between T_2A and T_3 (Fig. 1). As can be seen from the soil map, these mineralogical results indicate that this latter soil boundary should be situated about 100 feet west of the boundary mapped during the soil survey. Further evidence of this latter soil boundary is found in the fact that tourmaline forms quite a significant member of the mineral assemblages in the samples from S_4 onward, whereas it is absent from the surface soils above this point.

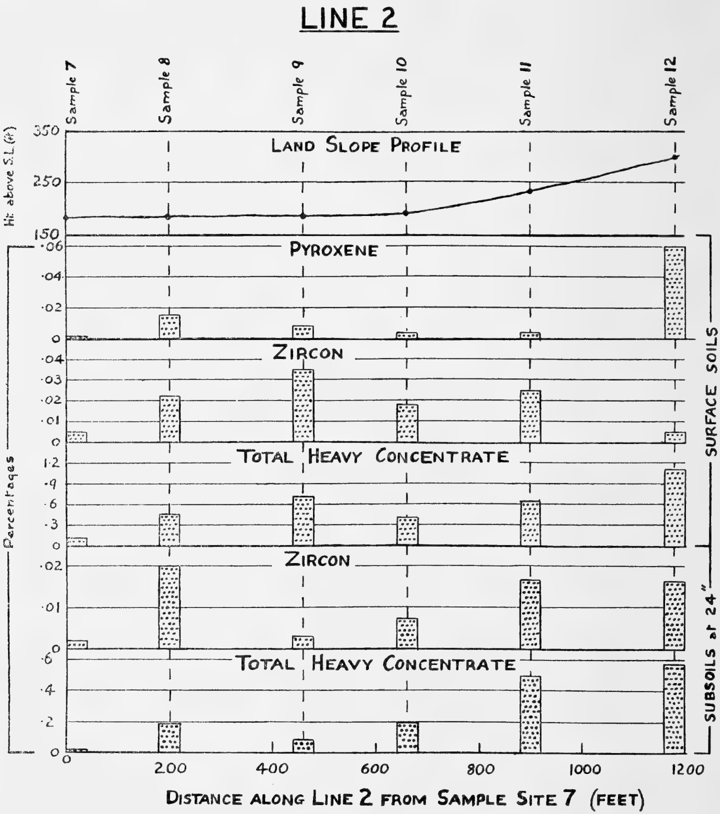

Fig. 3.

The histograms for Line 2 do not show such marked breaks in the type of parent material as do those for Line 1. There is a general but uneven rise in the percentage of heavy concentrate in both the surface soils and subsoils from the creek line up the slope. The pyroxene of the surface soil rises quite sharply between S_{11} and S_{12} and this does indicate a break at the point where contamination from the basaltic material has sharply increased. The subsoils all along Line 2 have very little or none of the basaltic type of pyroxene and so are probably not contaminated by the basaltic material, the contamination along this line being confined to the surface soils in which it is generally small but increases up the slope. Also, the subsoils contain a fairly even distribution of zircon along the whole line, indicating uniformity of parent material. Lastly, all the subsoils and surface soils contain tourmaline as a significant member of their mineral assemblages.

A possible explanation of the lack of uniformity in the trends of the histograms for Line 2 is that the line traverses several different soil types which are fairly closely related to one another but whose soil-forming processes, and possibly parent materials, may be sufficiently different to cause variations in the mineral assemblages. Several minor breaks are indicated by the histograms for both the subsoils and the surface soils, but the samples were insufficient in number and too widely spaced to assess accurately the significance of these small variations in mineral assemblage. The histograms of pyroxene for the surface soils and zircon and total heavy concentrate for the subsoils indicate a minor break between S_8 and S_7 which may possibly be explained by the influence of the creek at S_7. The break between S_{11} and S_{12} is a significant one, and it can be said with certainty that a soil boundary does exist between S_{11} and S_{12} and probably close to S_{12}, since at that point pyroxene is still low compared with the percentage of pyroxene in the soils of mixed origin on Line 1. This boundary corresponds to the boundary between T_2 and T_1 (Fig. 1).

DETERMINATION OF THE ADMIXING OF PARENT MATERIALS AND CONTAMINATION BY SOIL CREEP.

It is evident from the mineralogical analyses that the podsolised soils have been developed from parent material of a different origin from that of Black Earths. The geology of the area has been studied (Jones *et al.*, 1911) and the obvious conclusion is that the major portion of the parent material of the podsolised types has not been derived from the basaltic chilled margin of the intrusion. The possible sources of parent material for the podsolised types are, therefore, the Hawkesbury series and the Wianamatta series. The samples of sandstone and soil developed on shale (S_{13} and S_{14}) studied above have been taken as the most likely sources of parent material for these soils, since both occur within a few chains of the area.

A consideration of the histograms of Fig. 2 for Line 1 brings out several facts. One is that both the subsoils and surface soils of the podsolised types show a percentage of total heavy concentrate much greater than that of either the Triassic sandstone or the soil developed on shale. The surface soil at S_6 at the foot of the slope has 2·7% of heavy concentrate, which is the lowest for the surface soils on Line 1. The shale soil has only 0·12% and the Triassic sandstone 0·06% of heavy concentrate. Thus it should be possible, by accurate measurements of the percentages of various mineral species in the parent materials, the soil concerned, and the contaminating material, to evaluate the percentage of contamination of one parent material by another ; in this case of the parent material of the podsolised soil types (S_{13} and S_{14}) by the basaltic material from higher up the slope. A rough calculation based on the percentage of total heavy concentrate in the basaltic material, the soil developed on shale and the surface soil at S_6 showed a contamination of 20% of basaltic material in the surface soil of S_6. A similar calculation based on the pyroxene typical of the basaltic material gave a contamination of 6%, while the soil developed on shale had approximately the same percentage of zircon as the surface soil at S_6. Similar calculations for the subsoil at S_6 gave a contamination of 10% based on the total heavy concentrates and of 2% based on the pyroxene.

The variable results obtained from the above calculations indicate that several considerations have to be taken into account to obtain correct results. The first is the amount of weathering undergone by the pyroxene during the admixing and since then, due to soil-forming processes. This will reduce the amount of pyroxene now present as compared with the amount present in the contaminating material, and so the calculation based on the pyroxene is probably an underestimate. The second is the differential movement of grains of different specific gravity down the slope. Heavier minerals probably move more quickly than lighter ones and so contribute more to the contamination. The amount of this differential movement may or may not be significant. The third is the mean specific gravities of the various heavy concentrates. In the above calculations, based on the percentage of total heavy concentrate, the assumption was made that the mean specific gravity of all the heavy concentrates was the same. However, the contaminating minerals are probably largely the heavy opaques, so that the mean specific gravity has probably been underestimated, and therefore the percentage of contamination based on this method overestimated. The fourth is that the heavy liquid separations are not accurately quantitative, and this would especially upset any calculations based on the percentage of zircon, as it is present in relatively very small amounts.

The conclusions to be drawn from these considerations are that the method requires a series of quantitative separations to obtain accurately the percentage of heavy concentrate in each sample and to determine any differential movement of the various mineral species down the slope. The specific gravity of the contaminating and contaminated materials should be determined as accurately as possible. Calculations should be based on determinations made on a very resistant mineral such as zircon which is usually present in relatively small amounts, so adding to the necessity for quantitative separations. Further, it should be noted that, apart from any contaminating process, the soil-forming and weathering processes will result in a different percentage of all the heavy minerals in a soil than in the fresh unweathered rock, so that only weathered materials should be compared.

A further observation from the mineralogical analyses is that the surface soils of the podsolised types on Line 1 are richer in heavy minerals than the subsoils. The lowest heavy concentrate in the surface soils is $2 \cdot 7\%$ at S_6. The subsoil at this position has $1 \cdot 2\%$ of heavy concentrate. This indicates that apart from the original intermixing of parent materials on which the podsolised soils were developed a further contamination of the surface soil has occurred by soil creep down the slope. This contamination is probably still continuing, maintaining or even increasing the percentage of heavy minerals in the surface soils, while the percentage in the subsoils may be decreasing due to weathering processes. Evidence of soil creep and decreasing contamination with increasing distance from the source of the contaminating material is also seen in the decreasing percentage of heavy concentrate in the surface soils of the podsolised types, with increasing distance down the slope in Line 1. However, the percentage of heavy concentrate in the surface soils is consistently greater than that in the subsoils. This may be explained partly by the greater leaching due to the weathering processes in the surface soils.

Thus it can be deduced that the parent material of the podsolised soils consists of a mixture of material derived from the Triassic series and material derived from the basaltic chilled margin of the Prospect intrusion and that soil creep has further enriched the surface soils with material derived from the latter source. The amount of basaltic material in the mixed parent material has been estimated by the methods used as from 2% to 10% for the original parent material and 6% to 20% for the surface soils at S_6. The percentage for the surface soils increases up the slope.

The soil of the alluvial floodplain is very similar mineralogically to the surface soil at Site S_6 on Line 1. It has $2 \cdot 7\%$ of heavy concentrate, 4% of which is pyroxene derived from the basaltic material. It also contains a small amount of tourmaline derived from the Triassic series. The parent material therefore is again a mixture of Triassic material and basaltic material, but here the mixing is due to water action. The percentage contamination of the Triassic material by the basaltic material is probably the same as for the surface soil at S_6.

Recent History of the Area.

From these mineralogical considerations an attempt can be made to interpret the recent history of weathering along Line 1. The Prospect intrusion is known to have a steep contact with the Triassic series and to be intruded into that series (Jones *et al.*, 1911). Figure 4A gives some idea of the probable state of affairs immediately after intrusion. Denudation would then reduce the position to that shown in Fig. 4B. Further weathering and erosion would tend quickly to reduce the steep slope of the exposed chilled margin of the intrusion since this is basaltic in nature and so readily weatherable. The weathered basaltic material would spread itself down the slope, intermixing with the weathering Triassic series, giving rise to a state of affairs as in Fig. 4C, where there is an area of purely weathered basaltic material (A–A_1) beyond the boundary of the intrusion with the Triassic series. Below this occurs a mixture of basaltic material and Triassic debris (A'–A''). These are both underlain by the Triassic series. A–A'–A'' represents Line 1.

This interpretation is borne out by the mineralogical analyses. The hill crest consisted of Black Earths with heavy concentrate up to 13%, but decreasing down the slope as the depth of soil, and so the weathering effects increased (Fig. 2). Proceeding down the slope the area A–A' showed no sudden changes in mineral assemblage, but a gradual fall in percentage of heavy concentrate, and was underlain by a light grey clay with only $0 \cdot 11\%$ of heavy concentrate (S_{16}). At A' a sudden break in the histograms of Fig. 2 showed a change to the mixed Triassic and basaltic parent material.

Soils then developed on these parent materials when the hill slope had reached a stable condition. Further gradual erosion by the normal processes operating at the present time, principally soil creep, have resulted in an enrichment of the surface soils lower down the slope by basaltic material.

Summary and Conclusions

Soil samples were collected along two lines up a hill slope the top of which consisted of Black Earths developed on the chilled margin of an essexite intrusion and the lower slopes of podsolised soils developed on the Triassic series. Mineralogical analyses of the heavy concentrates of the surface and subsoils at two feet were made for these samples and the results plotted as two series of histograms together with the profile of the land form. For comparison, analyses were made of a Triassic sandstone, a soil developed on Triassic shale, the alluvial soil near a creek line at the foot of the slope and the deep subsoil below a Black Earth in the transition zone between the two types of parent material.

Examination of the resultant histograms showed several breaks in slope which indicated the presence of soil boundaries, definitely in the case of Line 1 but less obviously in the case of Line 2. Consideration of percentages of pyroxene and of heavy concentrate in the soils and in the samples from the Triassic series showed that the podsolised soils were developed on parent material of mixed origin and that the surface soils were being further contaminated by the process of soil creep. The alluvial soil was shown to be formed from similar mixed parent material. Quantitative estimates of the amount of mixing of parent materials were not possible because of the lack of precision in the methods used.

A general account of the recent history of weathering along Line 1 was deduced from the mineralogical studies in conjunction with the geological data available.

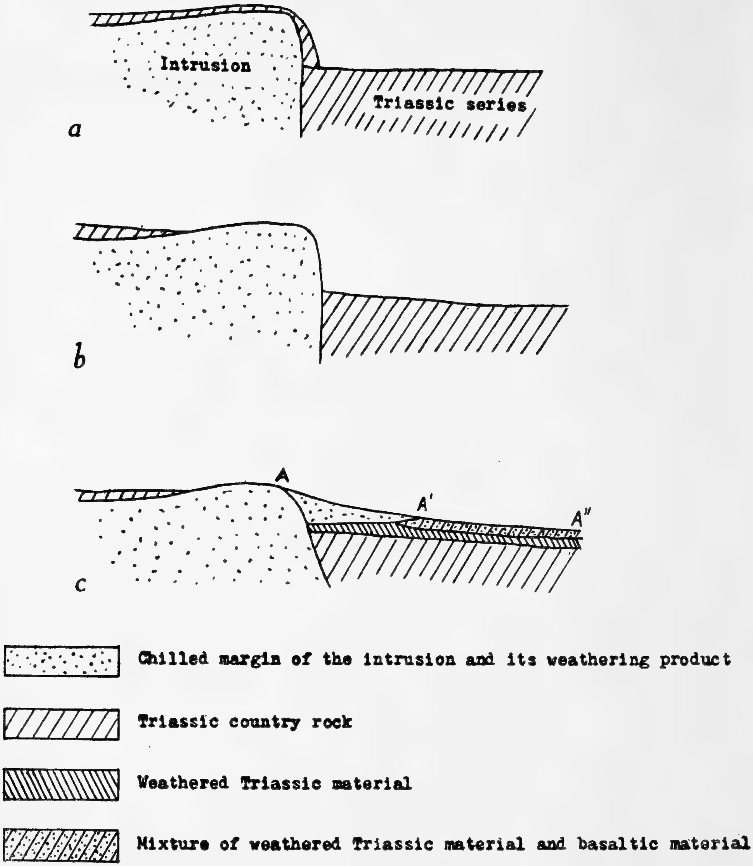

Fig. 4.—Illustrating the origin of soil material on the margin of the basaltic intrusion, Prospect Hill, N.S.W.

From these observations it has been concluded that mineralogical analyses can be used

(1) to determine the position of soil boundaries where they may not be very evident on the surface;

(2) to determine the recent history of weathering which, in general, has been neglected by both geologists and pedologists;

(3) to determine qualitatively the admixing of parent materials ;

(4) to determine quantitatively the approximate percentages of admixing of parent materials provided a quantitative method of separation is used and the calculations are based on the occurrence of a very resistant mineral such as zircon or tourmaline.

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RELATIONS OF RANK TO INHERENT MOISTURE OF VITRAIN AND PERMANENT MOISTURE REDUCTION ON DRYING.

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INTRODUCTION.

A definite relationship has been established between rank and moisture content for medium to high-rank coals (Dunningham, 1943 ; Gauger, 1932 ; King and Wilkins, 1943 ; Mott, 1943 ; Porter and Ralston, 1916 ; Rees, Reed and Lands, 1939). Moisture decreases with rank until about 88% carbon is reached, after which it increases again as rank becomes higher. Moisture varies within certain limits for coals of any particular carbon content, therefore the graphical relationship is of the nature of a zone within which coals fall when moisture is plotted against carbon. The zone is relatively narrow at about 88% carbon where moisture reaches a minimum, but it becomes wider as moisture increases towards both the anthracite and sub-bituminous rank-stages.

The well-defined minimum at the high-rank bituminous stage is regarded as an important feature in the moisture-rank relationship. It is at about this stage in rank advancement that coal attains its maximum caking and swelling properties, reaches a minimum in internal surface, develops marked anisotropism, and commences to show other chemical and physical changes which mark the first stages of anthracitization.

Results recorded for coals of rank lower than sub-bituminous show a very wide moisture-rank zone in the vicinity of the brown-coal stage, suggesting wide variation in moisture for any given carbon content when coals from different deposits are plotted on the same graph. In general, it has been inferred that moisture continues to increase as rank decreases from sub-bituminous coal, through the brown coals, to peat. This may be so if total bed-moisture is considered, because the texture of coal becomes increasingly open and spongy as the peat stage is approached, and the amount of adherent moisture which can be drained out by lifting it from the deposit, or squeezed out by pressing it in the hand, increases greatly. Such adherent moisture is merely lying in the bed and cannot be considered to bear any relation to the physical condition of the coal substance making up the individual fibres and pieces of plant material in the brown coal or peat.

Investigations described in this paper deal with the moisture actually adsorbed by the coal substance, and it is believed that results have established the existence of a maximum in the moisture-rank zone at about 67% carbon. The maximum appears to be well-defined, and it is probable that it corresponds with important changes in the development of micelle structure during rank advancement.

An investigation was also made of relations between rank and permanent changes in moisture content due to drying coals from their original water-saturated condition. Results of this work show that changes are greatest for coals with the highest inherent moisture contents, and that coals cease to undergo permanent changes after a certain rank-stage is reached.

Relations of Maximum Inherent Moisture to Rank.

Materials used in this investigation consisted of vitrains separated by hand from lump-specimens of coal ranging in rank from semi-anthracite to sub-bituminous, and the woody precursors of vitrain in the case of lower rank coals. The general nature of the materials, and their chemical properties, are summarized in Table 1.

Table 1.

Results of Investigation of Moisture-Rank Relations.

Spec. No.	Locality.	Geol. Age.	Rank.	Chem. Props. (A.F.D. Basis.)		Max. Inher. Moist. % (A.F.D.)	Ash % (D.C.).
				% Carbon.	% Vol. Cont.		
208	Baralaba, Q'land ..	Perm.	Semi-Anthr.	91·6	10·6	3·22*	1·98
28	Mittagong, N.S.W. ..	Perm.	Semi-Anthr.	91·5	7·4	3·93*	5·74
161	York Plains, Tasmania	Trias.	Semi-Anthr.	90·3	11·7	4·06*	3·61
310	Greta Seam, Aberdare, N.S.W.	Perm.	High-rank bitumin.	89·2	39·5	4·00*	1·52
312 314	Bulli Seam, Coalcliff, N.S.W.	Perm.	High - rank Bitumin.	88·6	22·9	1·88	0·90
30	Top Seam, Sydney, N.S.W.	Perm.	High - rank Bitumin.	88·3	23·5	3·21*	1·03
312	Bulli Seam, Helensburgh, N.S.W.	Perm.	High - rank Bitumin.	88·0	24·9	1·82*	0·81
460	Wallarah Seam, Wallarah, N.S.W.	Perm.	Bitumin.	84·1	33·3	5·77	1·32
458	Victoria Tun. Sm., Red Head, N.S.W.	Perm.	Bitumin.	83·7	36·9	4·01	2·59
459	Gt. Northern Seam, Belmont, N.S.W.	Perm.	Bitumin.	83·4	37·6	4·81	1·79
288	Wonthaggi, Victoria ..	Jur.	Bitumin.	82·0	34·4	13·35	1·19
124	Mt. Nicholas, Tasmania	Trias.	Bitumin.	81·9	34·6	18·23*	0·38
169	Borehole Seam, Wallsend, N.S.W.	Perm.	Bitumin.	81·3	34·4	5·55*	2·09
174	Liddell Seam, Liddell, N.S.W.	Perm.	Bitumin.	81·0	40·9	4·03*	2·99
212	Mt. Mulligan, Q'land. ..	Perm.	Bitumin.	80·7	29·7	6·93*	1·58
138	Wonthaggi, Victoria ..	Jur.	Bitumin.	80·3	38·2	15·43*	1·04
186	Seymour, Tasmania ..	Trias.	Bitumin.	80·0	36·5	10·20*	2·66
461	Wallarah Seam, Swansea, N.S.W.	Perm.	Bitumin.	79·8	36·3	6·10	6·45
143	Bluff Seam, Ipswich, Q'land.	Trias.	Bitumin.	79·1	35·5	4·53*	5·04
209	Callide, Q'land	Jur.	Bitumin.	77·9	36·8	21·45*	1·79
317	Griffin Seam, Collie, W. Aust.	Perm.	Sub-Bitumin.	76·6	32·9	26·20	2·38
120	Twelve Foot Seam, Collie, W. Aust.	Perm.	Sub-Bitumin.	74·8	34·7	26·00*	1·90
304	Leigh Creek, S. Aust. ..	Trias.	Sub-Bitumin.	74·5	36·2	67·50	3·83
457	Bovey Tracey, England	Tert.	Brown Coal.	70·5	54·4	61·45	1·87
456	Moosonee, Canada ..	Cret.	Brown Coal.	69·8	51·6	85·00	2·69
88	Berridale, N.S.W. ..	Tert.	Brown Coal.	68·9	53·8	78·82	3·20
454	Liblar, Germany ..	Tert.	Brown Coal.	68·3	54·7	94·60	1·39
136	Yallourn, Victoria ..	Tert.	Brown Coal.	67·4	60·1	118·30	1·79
455	Liblar, Germany ..	Tert.	Brown Coal.	62·5	64·6	69·30	1·79
104	Kiandra, N.S.W. ..	Tert.	Brown Coal.	59·2	76·4	61·30	0·43
453	Haltern, Germany ..	Pleis.	Peat.	58·2	87·7	38·75	0·31

* Values obtained by evacuation and resaturation of oven-dried vitrain.

The vitrains with carbon content higher than 74·5% were hard bright materials typical of normal vitrain. Those with less carbon were soft and dull with woody structure, and varied in colour from black to yellow-brown. Of these, the black materials containing approximately 68% to 74% carbon became hard and bright when dried, indicating that they were approaching the rank-stage at which soft dull woody lignite changes to hard bright vitrain under normal conditions of natural metamorphism (Dulhunty, 1946, 1948). The two pieces of woody lignite from the Cologne deposits in Germany (Nos. 454 and 455) were black and yellow-brown with carbon contents of 68·3% and 62·5% respectively. Materials, in Table 1, with 67·4% carbon and less were of yellow-brown colour, and although they became somewhat harder and more brittle on drying, they did not develop bright lustre.

Vitrains, and their woody precursors, were used so as to obtain results which would be comparable for coals containing different proportions of petrological constituents. This was considered essential as moisture contents vary considerably in the different banded constituents of coal.

Results described later in this paper indicate that vitrains containing less than 87% carbon undergo permanent reduction in maximum inherent moisture when dried, but those of higher rank are not affected in the same way and, if completely resaturated, will take up as much water as they held in their original saturated condition. As a result of this all vitrains with carbon content lower than 78%, used in the study of moisture-rank relationships, were materials which had been collected and maintained in their original water-saturated condition. In the case of coals of higher rank, some of the vitrains (marked with an asterisk in Table 1) were separated from specimens which had been allowed to air-dry as fresh water-saturated materials were not available, but after separation they were thoroughly evacuated and resaturated, by the method described later in this paper, before determining maximum inherent moisture.

Results for inherent moisture, carbon and volatiles are quoted as percentages of the dry ash-free vitrains. They were not recalculated according to any of the ash-correction formulas. The ash contents of materials with less than 77% carbon was so low, mainly between 1% and 2%, that the influence of mineral matter would be negligible. Vitrains with more than 77% carbon were saturated with water, then treated with a 5% solution of hydrochloric acid, and finally washed with water until acid-free. This removed mineral matter adhering to the vitrain particles, and reduced ash contents to between 1% and 3% in all except three cases where the ash contents were between 4% and 6% (see Table 1).

The values for moisture (Table 1) represent *maximum inherent moisture* determined by *controlled vaporization of adherent moisture* using the apparatus and technique described in an earlier publication (Dulhunty, 1947). Moisture contents determined in this way approximate very closely to absolute values for inherent moisture contained in all pores small enough to lower the vapour pressure of water, and which are considered to be part of the essential micelle structure of the coal substance. Adherent moisture with normal vapour pressure, contained in macroscopic cracks and openings, is removed during the process of determination. Values for maximum inherent moisture determined by this method are comparable for coals of all ranks and textures, and they are considered to be the most satisfactory for investigating relations between moisture and rank. Methods involving partial drying of coal, followed by resaturating in an atmosphere of water vapour under a pressure equal to the vapour pressure of water at the temperature employed, are not suitable as low rank coals undergo irreversible changes on drying. Results representing total moisture in the coal, as mined, are likely to be misleading owing to the presence of large amounts of adherent moisture in the case of some low-rank coals, and the fact that the natural bed moisture may be less than the maximum inherent moisture, producing "dusty conditions" in underground mines, in the case of some high-rank coals. Dunningham's Blotting Paper Method (Dunningham, 1943) gives significant results, but the standard amount of drying must be varied for coals of different ranks and textures, and this introduces difficulties when inherent moistures are to be compared in coals ranging from peat to anthracite.

The foregoing procedure consisted of the use of low-rank coals in their original water-saturated condition to avoid changes due to drying ; the separation of pure vitrain to avoid the influence of different proportions of petrological constituents ; and the use of a method of moisture determination which eliminates adherent moisture without any preliminary drying effects. This was adopted with the object of obtaining moisture results closely related to the physical condition or rank of the coal substance.

Results for carbon content and maximum inherent moisture, listed in Table 1, were plotted graphically as shown in Fig. 1. Curves drawn approximately at the upper and lower limits of the points, represent the zone within which the vitrains fall, or the zonal relationship between maximum inherent moisture and rank. The broken lines above 93% carbon, representing the extension of the zone into anthracite rank, are based on the results of previous investigators (references cited earlier). Vitrains with carbon contents of 74·5% and higher, plotted on the diagram, are Australian materials from all States except the Northern Territory ; their geological ages range from Permian to Jurassic, and the metamorphic conditions under which they have been coalified vary considerably. The moisture-rank zone for these materials becomes very narrow and reaches a minimum at about 88% carbon, which agrees with the relationship previously established for coals from other countries.

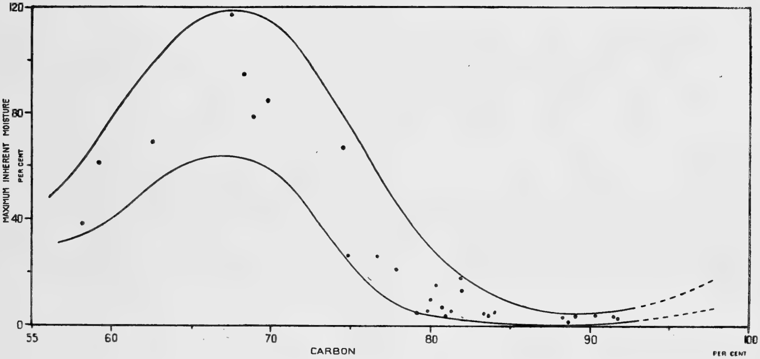

Fig. 1.—Diagram illustrating zonal relationship between maximum inherent moisture and rank of vitrain.

On the low-rank side (55% to 75% carbon) of the diagram in Fig. 1, there is evidence of a prominent maximum at about 67% carbon. This maximum does not appear to have been recorded by previous investigators, and it is believed that it is an important characteristic of the moisture-rank relationship. It occurs at immature brown-coal rank, and probably corresponds to the maximum degree of colloidal development attained during coalification, suggesting that the substance of wood undergoes a slow process of physical disorganization during the peat stage to become a watery gel at about immature brown-coal stage, where inherent moisture reaches its maximum. Decrease of inherent moisture on the high-rank side of the maximum would seem to be associated with the closing up, or maturing, of the micelle structure in the gel as physical rank is advanced by pressure from overlying beds and moderate earth temperatures operating over long periods of time.

The results indicating a maximum in the moisture-rank zone, on the low-rank side of Fig. 1, were obtained for woody materials occurring in brown coals in England, Germany, Canada and Australia, and ranging in geological age from Cretaceous to Pleistocene. This, together with the continuity of the zone throughout all ranks, and the agreement between zones for Australian vitrains above 74% carbon and for coals of similar rank from other countries, indicates that the same general moisture-rank relationship applies to all coals irrespective of their position in the world, the botanical species of original organic debris from which they were formed, or the exact conditions of metamorphism under which they were coalified.

The zonal nature of the moisture-rank relationship appears to be a consequence of independent advancement of physical and chemical ranks (Dulhunty, 1947*a*). In constructing the moisture-carbon graph, a factor associated with physical rank is plotted against one depending on chemical rank. The two ranks advance at the same time, but either may become more advanced than the other depending on conditions of metamorphism. This gives rise to a certain variation in moisture values for coals of any given carbon content, resulting in a zonal relationship. It follows that the varying width of the zone may be regarded as an expression of the extent to which chemical and physical ranks may differ in advancement during coalification.

RELATIONS OF RANK TO PERMANENT REDUCTION OF MOISTURE ON DRYING.

Results of previous work have shown that low-rank coals undergo permanent changes in hardness, lustre and inherent moisture when dried from their original water-saturated condition (Dulhunty, 1946 and 1948). The present investigation was undertaken with the object of determining the range in rank over which permanent reduction in moisture takes place when vitrain is dried, and also the relationship between the extent of reduction and rank.

Vitrains used were those, listed in Table 1 and included in Fig. 1, which had been collected and maintained in their original water-saturated condition. Maximum inherent moisture in the original water-saturated condition had already been determined in connection with work described earlier. Additional portions of the same vitrain samples were oven-dried at 105° C. in a stream of dry nitrogen until their weights were constant. They were then evacuated for one hour at room temperature using a vacuum pump capable of reducing pressure to 0·0003 mm. of mercury. The evacuation was carried out in a tube connected by means of a carefully ground glass cock to a vessel containing air-free water and water vapour. After pumping down for one hour, the vacuum line was shut off and the cock connecting with the air-free water was opened, allowing water vapour and liquid water to enter the tube containing the evacuated vitrain. When the vitrain was thoroughly wet and covered with water, the tube was opened and air allowed to enter. The vitrain was then allowed to stand under water for 24 hours, before draining and filling into the conditioning tubes of the apparatus for determination of maximum inherent moisture by controlled vaporization of adherent moisture.

Results for maximum inherent moistures determined on the vitrains in their original water-saturated condition, and after having been oven-dried and resaturated, are summarized in Table 2. It is evident that all materials with carbon contents of 76·6% and lower underwent marked reduction of inherent moisture as a result of drying. Those with carbon contents higher than 76·6% do not appear to have suffered any such change, as the two moisture values for each vitrain are within the limits of reproducibility for the method of determination (Dulhunty, 1947). Therefore it was concluded that vitrains containing more than about 78% carbon do not undergo permanent reduction of inherent moisture when oven-dried.

It has been suggested that all coals suffer a certain amount of permanent reduction in inherent moisture when oven-dried. As a result of the foregoing work it is believed that vitrains containing more than 78% carbon, and probably all coals of similar rank, can be oven-dried and resaturated to their original maximum inherent moistures if the drying is carried out in an atmosphere of nitrogen; if resaturation is sufficiently complete, and if the moisture values represent true inherent moisture and not varying amounts of adherent moisture.

TABLE II.

Relations between Rank and Permanent Reduction of Moisture on Drying.

(For further data, see Table I.)

Spec. No.	Carbon %. (A.F.D.)	Max. Inher. Moist. % (A.F.D. Basis).	
		Original Water-Saturated Condition.	Oven-dried and Re-saturated.
312–314	88·6	1·88	1·90
460	84·1	5·77	5·74
458	83·7	4·01	3·92
459	83·4	4·81	4·68
288	82·0	13·35	13·36
461	79·8	6·10	6·10
317	76·6	26·20	22·55
304	74·5	67·50	33·70
457	70·5	61·45	20·95
456	69·8	85·00	31·40
88	68·9	78·82	29·95
454	68·3	94·60	49·50
136	67·4	118·30	37·70
455	62·5	69·30	43·20
104	59·2	61·3	32·55
453	58·2	38·75	36·90

In previous publications (Dulhunty, 1946, 1948) it was suggested that low-rank coals undergo permanent reduction of inherent moisture on drying as a result of deformation of the micelles, and reduction of intervening spaces, under the influence of attractive forces between the micelles when internal pressure of adsorbed water is released by drying. From the present results it would appear that medium to high-rank vitrain, containing more than about 78% carbon, has reached a degree of maturity at which the micelle structure is sufficiently rigid to withstand the forces of inter-micelle attraction without deformation when adsorbed water is removed.

The relationship between rank and extent of permanent reduction of inherent moisture on drying is illustrated in Fig. 2. This diagram was constructed by plotting moisture values against carbon for each of the materials in Table 2. In the case of vitrains which showed permanent reduction, values for maximum inherent moisture in the original water-saturated condition and after oven-drying and resaturating are joined by vertical lines which indicate the extent of permanent reduction. Vitrains which did not undergo permanent reduction are shown as single points on the diagram. Curves were drawn through the two sets of points for vitrains showing permanent reduction. These curves form a zone the width of which represents approximately the amount of permanent reduction suffered by vitrains of different rank up to about 87% carbon. At this rank the two curves meet, and a single line drawn through the vitrains of higher rank indicates no permanent reduction of moisture on drying.

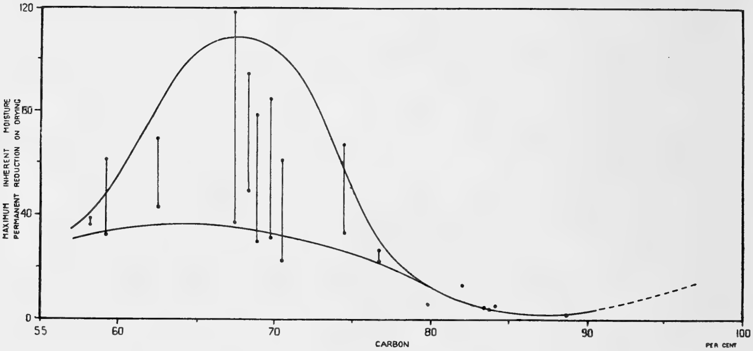

Fig. 2.—Diagram illustrating relationship between rank and extent of permanent reduction of moisture on drying vitrain, and range of rank over which permanent reduction takes place.

The complete diagram (Fig. 2) illustrates the range of rank (approximately 55% to 78% carbon) over which vitrain undergoes permanent reduction of inherent moisture on drying, and also shows that the amount of reduction for low-rank vitrain is related to rank. It is evident that the amount of reduction is greatest at the rank-stage where inherent moisture reaches its maximum in the moisture-rank relationship (Fig. 1). This supports the conception, discussed earlier, that vitrain attains its maximum degree of colloidal development at the rank where maximum inherent moisture is greatest. The watery gel formed at that rank, with soft immature micelle, would provide the optimum conditions for deformation of micelles, closing up of inter-micelle spaces, and the formation of larger inter-micelle contact areas, as a result of attractive forces operating when adsorbed water is removed by drying.

Summary of Results.

As a result of investigations outlined in this paper, it is concluded that :

(1) The relationship between maximum inherent moisture and rank of vitrain is characterized by a minimum in moisture at about 88% carbon (as previously established for coal samples), and a maximum in moisture at about 68% carbon (not previously recognized).

(2) Vitrains with carbon contents varying from about 55% to 75% undergo permanent reduction in maximum inherent moisture when oven-dried. Those of higher rank are not effected in this way.

(3) The extent of permanent reduction in inherent moisture increases with rank to about 67% carbon where it reaches a maximum. It then decreases to zero at about 78% carbon.

(4) The maxima reached by inherent moisture and permanent reduction of moisture on drying (at about 57% carbon) are both a consequence of a maximum in the degree of colloidal development attained by vitrain at the same rank.

ACKNOWLEDGEMENTS.

In conclusion the author wishes to acknowledge facilities provided from the Commonwealth Research Grant to the University of Sydney ; helpful discussion with Dr. D. H. Bangham, British Coal Utilisation Research Association ; and the assistance of Miss N. Hinder, B.Sc., in laboratory work.

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THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

PART XI. THE POTENTIAL OF THE TRIVALENT-QUADRIVALENT RHODIUM COUPLE IN SULPHURIC ACID.

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Grube and co-workers (1937) studied the electrolytic oxidation of rhodium III salt solutions and measured the potential of the system

$$Rh^{IV}+e \rightarrow Rh^{III}$$

The potential was found to vary from 1·363 volts in 0·154 N sulphuric acid to 1·434 volts in 1·00 N acid, and was notably unsteady in all acid concentrations, so that the final value quoted was 1·4 volts. In the present investigation the aim was to measure the potential more accurately and in solutions of greater acid concentration so as to obtain some insight into the form of the higher valent state.

Cells of the following types were measured.

$$Hg \mid Hg_2Cl_2 \text{ sat. } KCl \mid\mid NH_4NO_3/KCl \mid\mid Rh^4/Rh^3/H_2SO_4 \mid Pt$$

The potential of the saturated calomel electrode was checked against a quinhydrone electrode in potassium hydrogen phthalate at pH 4, and the value 0·2443 volt at 25° C. accepted. The cell assembly was similar to that used in previous determinations (Dwyer, Nyholm and McKenzie, 1944).

Since the system was found to be very slow in reaching equilibrium, as noted by Grube (*loc. cit.*), cerous sulphate was added as a potential mediator. This mediator was chosen since the redox potential of the cerous-ceric couple in sulphuric acid (1·45 volts) is close to the system being measured. One drop only of 0·0875 M solution in 0·2 N sulphuric acid was found to cause the potential to rise rapidly. Addition of further cerous salt did not affect the potential, but large amounts (1–2 c.c.) caused the potential to fall. In the presence of the mediator a steady potential was reached in 24 hours, and was not affected by stirring the solution. Curiously enough, the system was light-sensitive, the illumination from a 50-watt lamp at a distance of two feet causing the potential to fall by four or five millivolts. In the dark the potential rose immediately to the original value. All the measurements have been carried out in the darkness or in diffuse light.

The system was also found to be badly "poised", and the potentials were therefore determined with a valve potentiometer. With the Leeds and Northrup Type K potentiometer the potential fell very rapidly, whilst measurements were being made, finally coming to equilibrium 150 to 200 millivolts below the initial reading. If the lead from the platinum electrode was disconnected, however, the potential rose again slowly—more rapidly if the solution was vigorously stirred—and the initial high potential was reached in about 30 minutes.

The rhodium III sulphate in sulphuric acid of the appropriate concentration was oxidized, so that approximately half of the rhodium was in the quadrivalent state, in order that the correction for lack of equimolarity of the oxidized and reduced forms would be as small as possible. The potential on the bright platinum electrode in the presence of the mediator was determined, and when equilibrium had been reached the solution was immediately titrated potentiometrically with ferrous sulphate solution. Experiments showed that the loss of rhodium by diffusion during the anodic oxidation to rhodium IV was very small, and hence the amount of rhodium III was taken as the total rhodium less the oxidized rhodium. The activities of the oxidant and reductant ions are not known, hence concentrations have been used in the calculations.

$$\text{Then } E = E_0 + 0{\cdot}05915 \log \frac{[Rh^{IV}]}{[Rh^{III}]} \text{ at } 25° \text{ C.}$$

The potential of the system was found to rise very sharply up to an acid concentration of 1 normal, and then in the range from 1 N to 6 N varied only from 1·43 v. to 1·440 v. In the lower acid concentrations the oxidized solutions appeared to be turbid and the low potentials are thus probably due to extensive hydrolysis and the separation of rhodium dioxide.

$$Rh^{IV+} + 2H_2O \rightarrow RhO_2 + 4H^+$$

The almost complete independence of the potential and the acid concentration at higher acidities is difficult to explain. As suggested by Latimer (1940), rhodium IV is unlikely to exist in solution as a tetrapositive ion, but could exist as the oxy ion RhO^{++}:

$$Rh^{IV} + H_2O \rightarrow RhO^{++} + 2H^+$$

Complex ion formation which should occur in the higher acidities and chiefly with the oxidant ion would lower the potential. It is evident that complex ion formation does not occur and the very slight rise in the potential must be due either to more complete reversal of the hydrolysis as shown in the first equation or alternatively to a change in the form of the oxy ion RhO^{++} to $Rh(OH)^{+++}$:

$$RhO^{++} + H^+ \rightarrow Rh(OH)^{+++}$$

There is evidence that the ion in iridium IV solutions, at present being studied, may exist in at least two forms, whilst Grube (*loc. cit.*) has noted that the colour of rhodium IV solutions may vary, and has ascribed the effect to hydrate isomerism.

EXPERIMENTAL.

Preparation of Solutions.

Rhodium III Sulphate. Approximately 1 g. of rhodium sponge was dissolved by fusion in potassium bisulphate, and the resulting bright yellow mass extracted with water and filtered from traces of undissolved metal. The hydroxide was precipitated from boiling solution with sodium carbonate, and after thorough washing dissolved in sulphuric acid. The rhodium was estimated by reduction with hydrazine in alkaline solution, and ignition in a reducing atmosphere, and subsequently the solution was adjusted to be M/100 with respect to rhodium and N/2 with respect to sulphuric acid.

Rhodium IV Sulphate. The rhodium III sulphate solution, 20–25 cc., was placed in a small sintered glass Gooch crucible, dipping into N/2 sulphuric acid in a small beaker, and the levels inside and out rapidly adjusted so that no flow of liquid took place through the membrane. With a stout platinum wire spiral anode, and a lead cathode, the oxidation was carried out until 40–60% oxidation had occurred. The solution in the anode compartment at this stage had become greyish green in colour.

Measurement of the Potential. The oxidized rhodium solution, 20 cc., was placed in the redox cell, followed by sufficient sulphuric acid to give the required acid concentration, and the volume then made up to 30 cc. with distilled water. The cell solutions were thus approximatelyM/300 with respect to the oxidant and reductant ions. After the addition of the cerous sulphate mediator the solution was stirred continuously until equilibrium was reached. The concentration of the oxidant ion was then immediately determined in the redox cell by titration with N/100 ferrous sulphate solution.

The values of the potential E and the corrected E_0 values are shown in Table I.

TABLE I.

Acid Conc.	Rh^3 gms.	Rh^4 gms.	E (obs.).	Correction.	E_0
0·5 N	0·0108	0·0098	$1{\cdot}377_5$	0·0025	1·380
0·7	0·0126	0·0080	$1{\cdot}412_5$	0·0115	1·424
1·0	0·0116	0·0090	$1{\cdot}428_3$	0·0067	1·435
2·0	0·0111	0·0095	$1{\cdot}433_0$	0·0041	1·437
3·0	0·0106	0·0100	$1{\cdot}437_4$	0·0016	1·438
4·0	0·0115	0·0091	$1{\cdot}423_8$	0·0062	1·439
5·0	0·0108	0·0098	$1{\cdot}437_5$	0·0025	1·440
6·0	0·01111	0·0095	$1{\cdot}436_3$	0·0041	$1{\cdot}440_4$

SUMMARY.

The potential of the trivalent/quadrivalent rhodium couple in sulphuric acid solution has been found to vary from 1·380 volts in 0·5 N acid to 1·440 volts in 6 N acid. There was no evidence of complex ion formation in the concentrated acid solutions, and the oxidant ion appears to be RhO^{++}.

ACKNOWLEDGEMENT.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD, N.S.W.

PART VII. GEOLOGY OF THE BOGGABRI DISTRICT.

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With Plate XIX.

(Presented by permission of the Under Secretary for Mines.)

Manuscript received November 9, 1948. Read December 1, 1948.

INTRODUCTION.

The area covered by this paper adjoins the Gunnedah-Curlewis district (Hanlon, 1948*a*) on the south and the south-western part of the County of Nandewar (Hanlon, 1948*c*) along the Namoi River to the east. It extends northwards to the old surveyed town of Turrawan on the Namoi River and includes all known outcrops of Permian strata within the North-western Coalfield, north of Gunnedah and west of the Namoi River.

The survey was in the nature of a reconnaissance. A telescopic alidade traverse was made from Boggabri Railway Station to the Triassic beds outcropping to the west of the town, in order to give accurate figures on which to base estimates of the thickness of the Permian strata.

TOPOGRAPHY AND ACCESS.

Boggabri is the most important town in the district. It is situated on the North-western Railway line, being 320 miles from Sydney and 823 feet above sea level.

Access by road is good and main roads connecting with Gunnedah, Narrabri and Manilla are trafficable in practically all weathers. However, many of the secondary roads which cross the black soil plains become impassable after any appreciable rains.

Physiographically, the Boggabri district can be divided into three main types. These are the extensive alluvial flats along the Namoi River and its tributaries, Cox's Creek to the south of Boggabri and Tulla Mullen Creek to the north; the gently undulating areas where the Triassic and Permian strata outcrop; and the group of hills which rise steeply about 300 to 400 feet above the general surrounding level and are composed of Lower Marine lavas. Mount Binalong is an exceptional feature. It is composed of Tertiary dolerite and basalt. The summit is the highest point in the district and is approximately 1,700 feet above sea level.

GEOLOGY.

The geological formations comprise the following, which will be described in order, commencing with the oldest.

Tertiary to Recent alluvium.
Tertiary Igneous Rocks.
Triassic.
Permian—
  Upper Coal Measures—Booroomin Group.
  Lower Marine Series—Boggabri Volcanics.

Permian.

Only portion of the Permian sequence is present in the Boggabri district. The Lower Marine Series is represented solely by lava flows and the Upper Coal Measures is the only group of sedimentary beds which is definitely present. The Upper Marine Series may be represented, although there is no fossil evidence to support the suggestion. The Lower Coal Measures do not appear to outcrop.

Lower Marine Series. The Lower Marine lava flows which outcrop in the vicinity of Boggabri have been named the Boggabri Volcanics (Hanlon, 1948*c*). West of the Namoi River they consist mainly of rhyolites and felsites. At a few points, as for example at the foot of Robertson's Mount, rhyolites pass laterally into pitchstones. Near The Rock, in portion 145, Parish of Bogabri, County of Pottinger, the pitchstone appears to be in the form of a dyke intruding a more basic flow, which is much weathered at the present time. The dyke must have been intruded in a very fluid condition and reached close to the surface in order to account for the rapid cooling necessary to form the pitchstone. It is also unlikely, for the same reason, that any large amount of magma flowed through the channel.

Amygaloidal basalts occur in places, but are subordinate to the more acid types, at least as far as can be judged from outcrops. There appears to be a consistent diminution in the proportion of basalts in the Lower Marine sequence, as the beds are traced in a north-westerly direction. In the Werrie Basin (Carey, 1934, 1935) the Werrie Basalts preponderate, at Gunnedah the basalts and acid lavas are both well represented, while near Boggabri the acid lavas form the great bulk of the outcrops.

Upper Coal Measures. It is proposed to name the Permian sedimentary rocks the Booroomin Group, because the best section of them is obtained on a property of that name, to the west of Boggabri. The upper part of the sequence is exposed on hillslopes and the lower beds outcrop between there and the township of Boggabri. Some details of the lower beds can also be obtained from a bore sunk on " Booroomin ", in portion 175, Parish of Bogabri. At other points in the district only the upper beds are exposed.

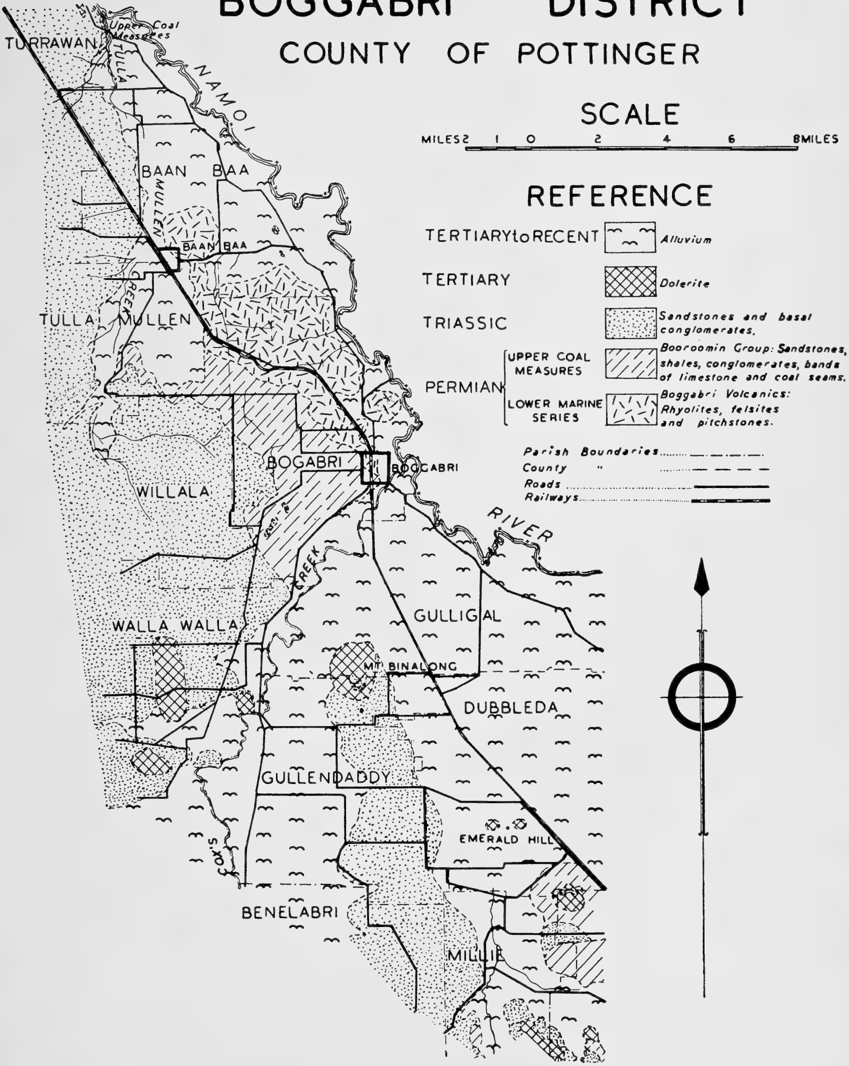
It is difficult to give an accurate estimate of the thickness of the Booroomin Group. The difference in height between the basal beds near Boggabri Railway Station and the base of the Triassic west of the town is 400 feet. The dip of the uppermost beds is generally in a west-south-westerly direction at between 1 in 100 and 1 in 30. If it be assumed that the dip is constant between " Booroomin " and Boggabri, the figures quoted would give a thickness for the Booroomin Group ranging between 550 and 900 feet. The bore referred to above is located 250 feet below the base of the Triassic and passed through 520 feet of sediments, allegedly striking 8 feet of coal at a depth of 502 feet. This would give a total thickness for the Booroomin Group in excess of 770 feet. Whatever the maximum thickness may be, the thickness at different places varies considerably, the sediments having been laid down on the eroded surface of the Lower Marine lavas.

The Booroomin Group is composed of sandstones, conglomerates, shales, thin limestone bands and coal seams, but the sequence differs materially from that of the type section of the Upper Coal Measures at Gunnedah. The topmost beds comprise sandstones and conglomerates, 60 to 70 feet thick. The pebbles in the conglomerates consist mainly of acid lavas, but some of the pebbly bands in the sandstones contain appreciable quantities of white quartz pebbles. This zone is underlain by shales containing *Glossopteris* and the weathered spoil of coal occurs on two horizons about 15 feet apart. Beneath the coal there are about 60 to 70 feet of shales and sandstones. The underlying beds form poor outcrops and as far as can be judged, comprise shales with bands of sandstone

Journal Royal Society of N.S.W., Vol. LXXXII, 1949, Plate XIX

GEOLOGICAL MAP BOGGABRI DISTRICT

COUNTY OF POTTINGER



and impure limestone. The latter are concretionary, at least in part. These beds are in turn underlain by sandstones and conglomerates, which rest directly on the eroded surface of the Lower Marine lavas near the town of Boggabri. The pebbles in the basal beds are composed of acid lavas similar to the underlying Lower Marine flows. The bore in portion 175, as far as can be judged from the log provided, passed through sandstones and shales to a depth of 422 feet, then through 69 feet of conglomerates, 11 feet of sandstone, 8 feet of coal and 10 feet of shales. However, as it was a percussion bore and the drillings were not examined by a geologist, too much reliance could not be placed on the log supplied.

The position of the upper coal horizon in fossiliferous shales, underlying sandstones and conglomerates containing bands of white quartz pebbles, suggests that it may be developed on or close to the horizon of Hoskisson's Seam, although it is only 100 feet below the base of the Triassic instead of about 240 to 300 feet below as in the type area at Gunnedah (Hanlon, 1948*a*). This would mean that, as at Breeza (Hanlon, 1948*b*), the upper portion of the sequence in the type area, that is, above the sandstone with the white quartz pebbles, is missing in the Boggabri district.

The increased thickness of the beds when compared with the sequence in the Gunnedah area, especially if the upper portion of the sequence be missing, would suggest that some of the lower beds may be of Upper Marine age. The zone of shales with sandstone and impure limestone bands, overlying a zone of conglomerates and sandstones, is also suggestive of the Upper Marine sequence at Gunnedah. The coal in the bore in portion 175, 750 feet below the base of the Triassic and 650 feet below the upper seam, does not correspond to coal developed anywhere in the Gunnedah area, unless a thickening of the intervening beds is postulated. This also raises the suggestion that this coal could form part of the Lower Coal Measures, developed below Upper Marine beds. However, a careful search of the beds failed to reveal any marine fossils, and in these circumstances it is considered advisable to classify all the beds as Upper Coal Measures.

Several bores sunk for water between Gunnedah and Boggabri have struck coal. The alluvium and perhaps some of the lower parts of the hillslopes, east of the Triassic beds in this area, are probably largely underlain by the Upper Coal Measures. North-west of Boggabri the coal measures can be traced as far as Tulla Mullen Creek, in portion 77, Parish of Tulla Mullen. The only outcrop north of this point is a restricted occurrence about ten miles downstream along Tulla Mullen Creek, near its junction with the Namoi River in the Parish of Turrawan, County of White. The beds underlie Triassic conglomerate, but the only fossil evidence found was very abundant silicified wood. Coal is alleged to have been struck in a bore on the creek flat near by, at a depth of about 80 feet.

Triassic.

The Triassic beds comprise the basal conglomerates with abundant jasper pebbles, which are so characteristically developed throughout the North-western Coalfield, and sandstones. Ferruginous altered rocks, which occur in portion 18, Parish of Gorman, County of White, have been identified as tuffs (?).

The basal conglomerates overlying the Upper Coal Measures sandstones, west of Boggabri township, form a massive bed, but are only about 20 feet thick. South of Mount Binalong the beds appear to weather easily and outcrops are represented by loose pebbles. At some localities, conglomerates seem to be developed on more than one horizon in the lower part of the Triassic sequence, and in portion 118, Parish of Gullendaddy, there appear to be three horizons of conglomerates separated by sandstones.

The overlying sandstones are thinly bedded and to the west and south of Boggabri form low escarpments in several places. However, over much of the area the sandstones form poor outcrops and much of the area underlain by these beds is covered with loose sand rising above the adjacent alluvial flats. This type of weathering to sandy wastes is very characteristic of Jurassic sandstones in many places. It raises the possibility that some of these beds may be of Jurassic age, although they could easily be Triassic sandstones which have weathered more completely owing to their having a different or inferior cementing agent in this section of the North-western Coalfield.

There is no fossil evidence on which to base an estimate of the age of any of the Mesozoic strata. The basal Triassic conglomerates do not outcrop between portion 77, Parish of Tulla Mullen, County of Pottinger, and portion 41, Parish of Turrawan, County of White, in which places they can be seen overlying Upper Coal Measures. It may be that the sandy wastes north of Baan Baa represent Jurassic sandstones which have overlapped the Triassic beds in the area. Near Baan Baa itself, although the Upper Coal Measures may occur beneath the alluvium, it is almost certain that they were overlapped in Mesozoic times, because Mesozoic beds are found within less than 50 chains of Lower Marine lavas that rise considerably above the level at which the sediments occur.

Tertiary Igneous Rocks.

The alkaline suite of Tertiary rocks, comprising rhyolites, trachytes, trachyandesites and andesites, which are found associated with the Boggabri Volcanics east of the Namoi River, appear to be absent, or if present, must form only a minor proportion of the outcrops.

The Tertiary igneous rocks mapped consist entirely of dolerites and basalts, and in most instances were intruded in the form of sills. The greatest thickness is at Mount Binalong, where the northern slope appears to be composed entirely of igneous material and would represent a total thickness of at least 900 feet. Specimens collected from the top of the mountain were monchiquitic in composition. Both olivine and analcite are abundant in the dolerites. Some of the amygdaloidal basalts associated with the Boggabri Volcanics may also be of Tertiary age.

Tertiary to Recent.

The only sedimentary deposits of these ages are the deposits of alluvium along the Namoi River and its tributaries. The largest expanse is along the Namoi River east of Mount Binalong and along Cox's Creek to the west. Around Boggabri, where the Namoi flows through the area occupied by the Lower Marine lavas, the alluvium is much restricted. Further north it widens again and there are considerable areas along Tulla Mullen Creek and along the Namoi River itself. The alluvium is of the " black soil " variety, similar to that described for other parts of the North-western Coalfield.

STRUCTURAL GEOLOGY.

The structure of the area represents the northerly continuation of the relatively simple structures of the Gunnedah area. Both folding and faulting are of a minor nature.

The area in which the Lower Marine lavas outcrop probably represented an old structural high to the east of which sedimentation took place in Lower Coal Measures time. West of this high the Lower Coal Measures were developed to a much lesser extent, if at all, and the Upper Coal Measures (and possibly Upper Marine Series) was laid down on the eroded surface of the Lower Marine lavas. The Triassic beds appear to overlie the Upper Coal Measures conformably. The Triassic (or possibly Jurassic) would appear to have overlapped the coal measures near Baan Baa and to have rested directly on the Lower Marine lavas. Whether the Triassic beds may have been overlapped in turn at some points it is impossible to say.

ACKNOWLEDGEMENTS.

I was assisted by Mr. J. C. Lloyd, B.Sc., and many helpful discussions with him during the course of the work are gratefully acknowledged. I am indebted to Mr. H. F. Whitworth, M.Sc., Curator of the Mining Museum, for the petrological determinations. I also wish to express my thanks to Mr. J. E. Lancaster, Under Secretary for Mines, and Mr. C. St. J. Mulholland, B.Sc., Government Geologist, for permission to publish this paper.

SUMMARY.

The Permian sediments comprise only the Upper Coal Measures, which have been deposited on the eroded surface of the Boggabri Volcanics (Lower Marine). The coal measures are overlain conformably by Triassic beds and Jurassic sandstones may possibly occur. The sediments have been intruded by Tertiary dolerite sills and there are also extensive alluvial areas. The structural geology is simple.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD, N.S.W.

PART VIII. GEOLOGY OF THE NARRABRI DISTRICT.

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With Plate XX.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION.

The Narrabri district comprises most of the northern half of the County of Nandewar, north of Maules Creek, together with small sections of the Counties of Jamison, Murchison, Pottinger and White. It adjoins the South-Western part of the County of Nandewar (Hanlon, 1948*a*) along Maules Creek, and the Boggabri District (Hanlon, 1948*b*), near the old surveyed town of Turrawan.

The geology of the area was described previously by Jensen (1907), who was mainly interested in the petrology of the Tertiary igneous rocks. Some of the boundaries between the sediments and the Tertiary igneous rocks have been adapted from his map. However, the classification of the Permian strata and their disposition and relationships with the Triassic and Carboniferous beds, as set out in this paper, are the author's work. The Narrabri district also overlaps, at one point, the area mapped by Benson (1917), east of the Nandewar Mountains.

The survey was in the nature of a reconnaissance. The rough terrain and the extensive Tertiary intrusions and lava flows, with resultant heavy talus cover on steep slopes, rendered accurate mapping of boundaries difficult and in some places impossible. The boundaries of the Permian with the Triassic and Carboniferous beds are accurate within the limits of the survey methods used except in areas where they have been intruded or covered by Tertiary igneous rocks.

TOPOGRAPHY AND ACCESS.

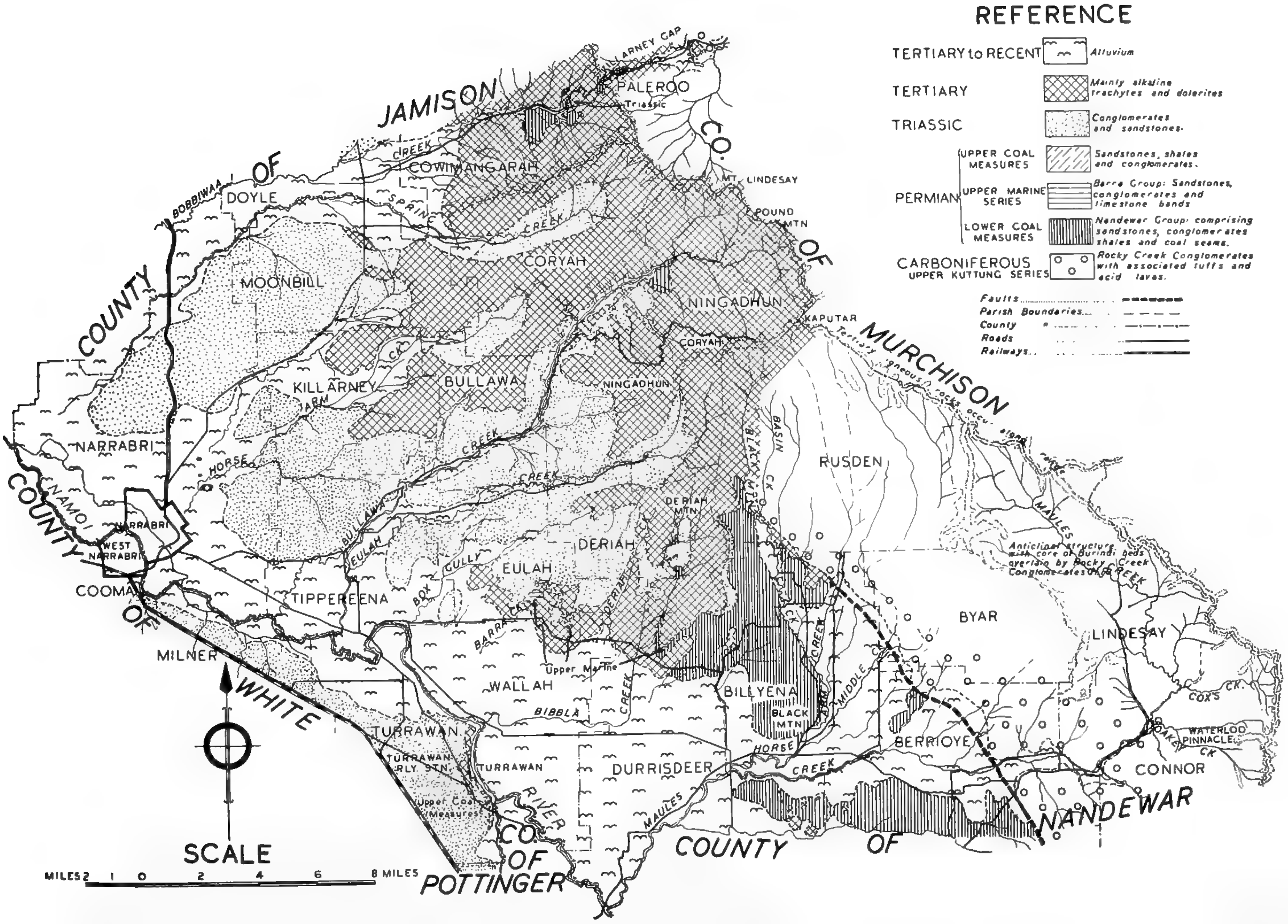
The only town in the district is Narrabri. (West Narrabri is adjacent to it and is located on the opposite or western side of the Namoi River.) The main part of the town is situated along Narrabri Creek, a tributary of the Namoi River. The North-western Railway line passes through the town and connects with Moree to the north and Boggabri to the south. Branch lines connect with Walgett and Pokataroo. Narrabri is 353 miles from Sydney and is 697 feet above sea level.

Access by road varies considerably. Over the flatter sections access is good, except that many of the roads become impassable after any appreciable rains. On the other hand there are very few roads in the mountainous section of the area and many points are accessible only on foot.

Topographical relief is considerable and the area can be divided into three main zones, a low-lying section, an intermediate zone, and the Nandewar Mountains proper. The low-lying section is mainly covered by alluvium and is situated along the Namoi River and the lower part of Maules Creek. Outcrops which rise above the general plain level reach only a moderate elevation. The

Journal Royal Society of N.S.W., Vol. LXXXII, 1949, Plate XX

GEOLOGICAL MAP
RECONNAISSANCE SURVEY
NARRABRI DISTRICT



intermediate zone is composed largely of Permian and Triassic beds, which have been intruded and in places covered by Tertiary igneous rocks. The surface slopes generally to the south-west, away from the main mass of the Nandewar Mountains. The creeks, which in the plains form only insignificant watercourses, tend to occupy narrow gorges, and ground suitable for cultivation is confined to a narrow strip along the floor of the gully. The Nandewar Mountains proper are composed mainly of igneous rocks and relief is considerable. The highest point is Mt. Kaputar, 5,000 feet a.s.l., and many peaks along the main line of the range rise well above the 4,000 feet level. A branch spur extends west-south-westerly from the vicinity of Mt. Kaputar, and on it the peaks Coryah, Yulludunida and Ningadhun are located.

GEOLOGY.

The geological formations comprise the following, which will be described in order, commencing with the oldest.

Tertiary to Recent alluvium.
Tertiary Igneous rocks.
Triassic.
Permian—
  Upper Marine Series—Barra Group.
  Lower Coal Measures—Nandewar Group.
Carboniferous—
  Upper Kuttung Series—Rocky Creek Conglomerates.

Carboniferous.

The Carboniferous beds form the northerly continuation of the Upper Kuttung beds mapped previously to the south of Maules Creek (Hanlon, 1948*a*). They are the equivalents of the Rocky Creek Conglomerates described by Benson (1917), and comprise conglomerates, which are often coarse, interbedded with tuffs and acid lavas. The rocks have not been studied in detail and only their western boundary has been mapped.

Permian.

The coal-bearing strata in the Narrabri District have always been regarded as belonging to the Upper Coal Measures. It now appears that they form part of the Lower Coal Measures and that the Upper Coal Measures are missing, being overlapped by the Triassic, which rests directly on Upper Marine beds. In the northern and eastern sections of the district, the Upper Marine seems to be overlapped in turn and it is likely, at least to the north, that the Triassic beds rest directly on the Lower Coal Measures. Lower Marine beds do not outcrop in the area and it is unlikely that the lavas of this age, found further south, are developed. However, if they were developed, the lack of outcrops could easily be explained as being due to their elimination by the faulting which occurs in the area.

Lower Coal Measures. The Greta age of these beds has been established by the discovery of Upper Marine fossils in the overlying beds. They represent the northerly continuation of the Nandewar Group (Hanlon, 1948*a*), which has been mapped to the south of Maules Creek. They comprise conglomerates, sandstones and shales with coal seams. Plant remains are very abundant on several horizons in the shales. Many of the fossiliferous bands are heavily iron-stained and contain ironstone concretions. Fossil wood is also very abundant, at times the wood being entirely replaced by ironstone. The best collection of fossil leaves was obtained from portion 47, Parish of Billyena, County of

Nandewar, on the southern slopes of Black Mountain. The following forms have been identified:

**Noeggerathiopsis hislopi* Feistmantel.
Glossopteris browniana Brong.
Glossopteris tortuosa Zeiller.
Glossopteris indica Schimper.
Glossopteris cf. *jonesi* Walkom.

The thickness of the Permian strata in the neighbourhood of the boundary between the Parishes of Billyena and Deriah must be at least of the order of 1,000 feet. Whether the upper section of these beds is of Upper Marine age it is not possible to say in the absence of any fossil evidence, and all the beds have been mapped as Lower Coal Measures. It is also not possible to say whether the whole of the Nandewar Group developed further south is represented in the area. The Wean Formation is certainly present, but the Vickery Conglomerates does not occur as such. The upper section of the sequence in portions 3 and 114, Parish of Billyena, is composed mainly of sandstones with conglomerate bands. No fossils were found in it and it could represent the Vickery Conglomerate. The change in facies would not need to be sudden, because the type area in which the Vickery Conglomerate is developed is 20 miles away. A careful search for fossils in the area may yield valuable information as to the easterly limits of the Upper Marine beds and also enable the age of the Vickery Conglomerate to be determined more definitely.

The most widespread outcrops of the Nandewar Group are in the Black Mountain Creek area. They are also well represented in the upper reaches of Bullawa and Bobbiwaa Creeks and their tributaries, and probably occur along the bed of portion of Eulah Creek, although no recognizable outcrops were seen. In areas which have been intruded by Tertiary igneous rocks, some blocks have been carried well above the positions they would occupy normally, and now occur above the level of adjacent Triassic beds. This applies particularly to the Killarney Gap area, coal measures outcropping along the divide where the main road between Narrabri and Bingera crosses the range, while *Thinnfeldia* has been found in shaley bands in sandstones at the foot of the mountains.

The only information available as to the thicknesses of the coal seams is that provided by wells and percussion bores. The outcrops of any seams examined were perished. In the absence of analyses or the availability of fresh samples for examination, it is not possible to form a definite opinion as to the quality of the coal. The general impression gained is that the seams would be of fair quality, but may only be thin.

Upper Marine Series. It is proposed to refer to the Upper Marine beds as the Barra Group, the maximum development of definite marine beds being north of Barra Creek, in portion 80, Parish of Eulah, County of Nandewar. It is impossible to obtain good sections of the beds or give any reliable figures for their thickness, because of the talus cover on steep slopes. In the type locality the beds are found over a range in height of several hundreds of feet. However, in an adjacent tributary creek they appear to be absent, the only outcrops below the Triassic being Tertiary dolerite. Further east in portion 78, Parish of Eulah, the beds are only a few feet thick, being overlain by Triassic conglomerate and underlain by Tertiary dolerite. The dolerite may extend westwards in the form of a sill or sills in the Upper Marine beds and account for a large proportion of the thickness over which they occur. It is probable that the maximum thickness is of the order of 200 feet.

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* There is a considerable variety in size in *N. hislopi* and more than one species may be represented.

The possibility that some of the beds mapped as coal measures further east may belong to the Upper Marine has been discussed above. If these beds should be Upper Marine, the maximum thickness would exceed the 200 feet quoted.

The most comprehensive suite of fossils was obtained from portion 80, Parish of Eulah, and comprised the following forms:

Protoretepora ampla Lonsdale.
Fenestrellina spp.
Spirifer duodecimcostata McCoy.
Terrakea brachythœra Sowerby.
Mœonia carinata (Morris).
Stutchburia compressa (Morris).
Edmondia nobilissima de Koninck.

Dun (1909) identified *Protoretepora*, *Spirifera*, *Mœonia carinata*, *Pachydomus* and *Ptychomphalina* in a collection of fossils by Mr. L. F. Harper, who probably obtained them from the same locality.

In portion 78, Parish of Eulah, the following forms were found in a band of impure limestone overlying a dolerite sill and within a few feet of the basal Triassic conglomerate.

Terrakea brachythœra (Sowerby).
Ptychomphalina morrisiana McCoy.

Conglomerates and sandstones occur in portion 11, Parish of Deriah, overlying coal measures, and in turn overlain by Tertiary dolerite. The following forms were collected from these beds.

Terrakea fragile (Dana).
Fenestrellina sp.
Spirifer duodecimcostata McCoy.

This occurrence is of particular interest because it proves the underlying fresh water beds belong to the Lower or Greta Coal Measures.

Triassic.

The Triassic rocks consist mainly of sandstones with basal conglomerates. Thin shaley beds occur, but form only a very minor proportion of the full sequence. The only fossil evidence as to their age was one poorly preserved specimen of *Thinnfeldia* sp. obtained from an outcrop on the side of the Killarney Gap road in portion 17, Parish of Cowimangarah, County of Jamison.

The basal conglomerates are similar to those developed in other parts of the North-western Coalfield, being characterized by the occurrence of jasper pebbles. However, in parts of the area the jasper pebbles do not preponderate to the same extent as further south. In the vicinity of Bibbla, Deriah, Bullawa and Eulah Creeks pebbles of acid lavas are abundant and the jasper pebbles are sometimes subordinate.

The overlying sandstones are several hundreds of feet thick and in places are very thinly bedded. This seems to be particularly the case with beds in the lower part of the sequence, close to the basal conglomerates. Higher in the sequence the beds are more massive. The Triassic sandstones are probably overlain by Jurassic sandstones and may be partly overlapped by them. The basal conglomerates, too, may be overlapped in places. North, south and west of Narrabri, Jurassic strata must have been deposited and would have connected with the Jurassic beds which outcrop between Narrabri and Warialda in one direction and Gunnedah and Coonabarabran in the other. How far easterly these beds extend it is not possible to say. At many points in the State, Jurassic sandstones weather easily to form sandy wastes, and this suggests that some of the low-lying areas composed of sandy wastes rising above the alluvium in the vicinity of Narrabri may represent Jurassic sandstones. However, there is no other evidence on which to base a determination of the age of the beds and it would be difficult to draw any satisfactory line of demarcation between the Triassic and what may be Jurassic beds. In the absence of any definite evidence of Jurassic strata in the area, the Mesozoic beds have all been shown as Triassic.

Tertiary Igneous Rocks.

They consist mainly of an alkaline suite of intrusives and extrusives and comprise porphyries, rhyolites, trachytes, andesites and basalts, together with a group of calcic rhyolites and basalts (Jensen, 1907). Tuffs and breccias are associated with them in places. The whole group of rocks has been described previously by Jensen, whose paper dealt mainly with their petrology.

The rocks occur as flows, dykes and sills, and often pass from one of these forms into another. The shape of the resulting igneous mass is complex and this, together with the abundant talus, which occurs on steep slopes, renders accurate mapping difficult and in some cases impossible. Mapping is further complicated by the occurrence of blocks of Triassic and Permian sandstone which have been " floated up " by the Tertiary intrusives.

Tertiary to Recent.

The only sedimentary deposits of these ages comprise alluvium and cemented gravels. The alluvium is largely of the " black soil " variety, although adjacent to the sandy wastes derived from the weathering of Mesozoic sandstones, it contains a fair proportion of sand.

The main development is along the Namoi River and in the Maules Creek-Bibbla Creek area. Very large alluvial areas lie north-west of Narrabri, beyond the limits of the area mapped.

STRUCTURAL GEOLOGY.

The boundary between the Carboniferous and the Permian beds is in the nature of a thrust fault. The zone of thrust faulting has now been traced continuously from the Werrie Basin (Carey, 1934), through the southern part of the County of Nandewar (Lloyd, 1933 ; Hanlon, 1948*a*), to the Nandewar Mountains.

The eastern thrust lies outside the area mapped and its exact location is a matter for conjecture. From a few scattered observations and the reported occurrence by Jensen (1907) of Devonian (?) cherts and slates near Waterloo Pinnacle in the Parish of Connor, County of Nandewar, it seems likely that the eastern thrust trends approximately parallel to the western thrust, which is shown on Plate XX, and passes close to Waterloo Pinnacle. North of this point there is little evidence on which to judge its position. It probably follows along or east of the spur which forms the divide between Maules Creek and the easterly flowing tributaries of the Manilla River. This spur parallels the western thrust and joins the Nandewar Range near Old Man Mountain. In the Parish of Lindesay, County of Nandewar, Raggatt (1931) recorded the occurrence of typical Burindi shales and conglomerates which extended eastwards to the divide, where they were covered with Tertiary volcanic rocks and westwards passed upwards into massive conglomerates, rhyolite and felsite (Rocky Creek Conglomerates.—F.N.H.). The structure was in the form of an anticline which was probably closed to the south. This would conform with the structure of the zone between the two thrusts further south, which is generally anticlinal.

The western thrust follows approximately a north-westerly trend, until it is obscured by the Tertiary igneous rocks. For most of the distance it is covered by alluvium. It probably lies some little distance in front of the line of Carboniferous hills, because, where the coal measures outcrop and its position can be estimated with reasonable accuracy, this is the case. From the point between Black Mountain Creek and its tributary Basin Creek, in the Parish of Rusden, County of Nandewar, where the fault is obscured by Tertiary igneous rocks, it must swing away to the north. If it continued on a north-westerly trend it would cross Eulah and Bullawa Creeks and could not fail to be identified. Jensen (1907) recorded mainly trachyte with some sandstone on the western fall at the head of Bullawa and conglomerates (Rocky Creek conglomerates according to Benson (1917)) on the eastern fall at the head of Boomi Creek. It is probable that the fault follows along the range at this point, being covered by the Tertiary igneous rocks. Further north at Nobby's, in the Parish of Paleroo, County of Murchison, a fault again forms the boundary between the Carboniferous and the Permian and probably represents the continuation of the western thrust.

As to the age of the thrusting, all that can be said with certainty is that it is post-Lower Coal Measures. From a study of adjacent areas, it is clear that the thrusting post-dates the Upper Coal Measures. The upper limit to the age can be judged only from a consideration of general principles and it is proposed to leave the discussion of this point until a later date.

West of the zone of thrust faulting and away from the influence of any Tertiary intrusives or associated faulting, the dips are generally low and vary between south-westerly and westerly. This accounts for the change from Triassic to Permian beds as one proceeds up many of the westerly flowing creeks.

The relationship of the Triassic to the Permian appears to be that of a progressive overlap. In the Parish of Eulah, the basal Triassic conglomerate rests directly on the Upper Marine and the Upper Coal Measures, which form such prominent outcrops west of the Namoi River in the Boggabri and Gunnedah areas, are missing. Further east in the Black Mountain Creek area the Upper Marine beds were not recognized. In the north along a tributary of Bobbiwaa Creek, *Glossopteris*-bearing shales occur close to the base of the overlying Triassic beds, and it appears that the Upper Marine beds have been overlapped in turn.

Faulting was also associated with the intrusion of the Tertiary igneous rocks, and the faulting, combined with the " floating up " of masses of sediments on the Tertiary intrusives is considered to account for the occurrences of coal measures which lie above Triassic beds to the west. The Tertiary intrusions probably followed lines of weakness developed during the earlier folding and thrusting.

ACKNOWLEDGEMENTS.

I was assisted by Mr. J. C. Lloyd, B.Sc., and many helpful discussions with him during the course of the work are gratefully acknowledged. I am indebted to Dr. A. B. Walkom, Director of the Australian Museum, for the determinations of the fossil plants, and to Mr. H. O. Fletcher, Palæontologist to the Australian Museum, for the determinations of the marine fossils. I also wish to express my thanks to Mr. J. E. Lancaster, Under Secretary for Mines, and Mr. C. St. J. Mulholland, B.Sc., Government Geologist, for permission to publish this paper.

SUMMARY.

The Permian outcrops comprise only the Lower Coal Measures and Upper Marine Series. The Upper Coal Measures are overlapped by the Triassic. Carboniferous beds have been thrust against the Permian along their eastern boundary. Widespread igneous activity in Tertiary times resulted in the intrusion and extrusion of a comprehensive group of alkaline rocks.

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NOTE ON THE OCCURRENCE OF TRIDYMITE IN METAMORPHOSED HAWKESBURY SANDSTONE AT BUNDEENA AND WEST PYMBLE, SYDNEY DISTRICT, NEW SOUTH WALES.

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INTRODUCTORY.

It is well known that the Hawkesbury Sandstone, where penetrated by basic intrusions and volcanic vents, has been metamorphosed into quartzitic rocks. The degree of change varies greatly, so much so that in various occurrences all gradations from slightly indurated sandstone to almost completely recrystallized derivatives have been observed. It is rare, however, to find evidence of greatly elevated temperatures having operated in the contact metamorphic zone.

The nature of the metamorphism has not been thoroughly studied in any one locality, and little has been placed on record concerning the petrological details of the changes. Considerable reference has been made, however, to the megascopic structural features in the sandstone. Thus the prevalence of a prismatic shrinkage-structure has been commented upon and some occurrences have been illustrated and described in early geological papers.

It is clear from even cursory field-examination that two types of metamorphism have affected the Hawkesbury Sandstone:

(*a*) Purely thermal (non-additive) metamorphism has been operative, causing the baking of sandstone with some mineralogical and textural modifications.

(*b*) Addition of siliceous solutions has been associated with thermal change, contributing to the development of glassy, quartzitic derivatives.

DESCRIPTIVE.

The aim of the present note is to record the occurrence of *tridymite* in contact metamorphosed phases of the Hawkesbury Sandstone at Bundeena, near Cronulla, and at the road-metal quarry, West Pymble. During a recent visit with Mr. G. E. McInnes, Demonstrator in Geology, to the Bundeena locality, the author noted the rather unusual appearance of finely-textured prismatic quartzite which occurs immediately adjacent to a weathered basic dyke. The field-relations can be well studied at the locality of the Bundeena Ferry Wharf, which is served by launches from Cronulla.

Here the tectonic environment of the dyke-unit and the general metamorphic effects can be quickly perceived. It is clear that variable textural conditions of the original sandstone have contributed to selective silicification. Fuller treatment of the problems presented by these outcrops will be undertaken in the future.

The somewhat peculiar grey quartzitic rock has been studied microscopically. It contains a not inconsiderable amount of the somewhat rare mineral *tridymite*, a variety of silica.

The tridymite is found mainly in two ways:

(*a*) As small laths and tabular crystals forming irregular fringes to quartz grains, and

(*b*) as elongated crystals and tiny plates embedded in a partially glassy mesostasis.

In addition, some tridymite units are set in recrystallized potash felspar, and radial-fibrous (partly spherulitic) material is occasionally present.

The tridymite is almost wholly in the inverted condition of quartz. This is to be expected in view of the known data concerning the stability-ranges of the various forms of silica. The small quantity of non-inverted tridymite shows very low D.R. (0·003–0·004) and extinguishes parallel to the length of the crystal or fibre. Wedge and arrowhead twinning is sparingly developed. The tile or imbricate structure of this mineral (as reported in literature) is not present. The refraction is low (approx. 1·47) but the bulk of the material shows the refractive index and birefringence of quartz.

The arrangement of the fringe-minerals is most erratic, and in many, but not all, cases the fringe and plexus-material extinguish at the same time as the quartz grains to which the tridymite is attached.

The glassy patches are mostly of felspathic material, possessing a refraction greater than that of the pseudomorphed tridymite.

Some grains of quartz in the Bundeena rock have been completely recrystallized, producing aggregate-assemblages marked by very crenulated borders.

The rock from the contact in the Pymble quarry contains less tridymite than that from Bundeena, and this would appear to be related to

(*a*) the temperature in the aureole during metamorphism having been lower, and

(*b*) the original felspathic content having been small.

This view is taken because careful study of the Bundeena rocks shows that partial vitrification of the sandstone is achieved by the formation of a felspathic melt (with or without some added quartz). Such a melt has attacked the quartz grains with resulting solution leading to enrichment of the melt in silica. With fall of temperature the tridymite has crystallized in plates and rods embedded in yellowish or brownish glass.

Although the optical and crystallographic properties of the tridymite and of the inverted quartz are similar in the rocks of the two localities, a notable feature is that the extinction of rods and laths is not always straight (or parallel). One would expect straight extinction for quartz pseudomorphic after tridymite, if the elongation of the rods were parallel to the optic axis " c " of the quartz, or if the laths represented sections perpendicular to (0001 plates). The phenomenon of an inclined extinction of tridymite with angles up to 45 degrees puzzled Flett in his descriptions (1911) of buchite inclusions in a dolerite sheet in the Ross of Mull.

In the present investigation the tridymite-bearing rocks were taken from almost at the contact surface between dolerite and sandstone. Thin slices of a quartzitic rock taken about 30 feet from the contact in the Pymble quarry show no sign of tridymite.

GENERAL.

The present occurrences are in line with cases described from other parts of the world. Thus Harker (1939) has described and figured tridymite-bearing quartzite from the Torridonian Series of Rum, and his illustration (Fig. 21A) portrays exactly the manner of the occurrence at Bundeena. H. H. Thomas (1922) has described inverted tridymite fringes in buchite from Mull, and with

Hallimond (1920) has described the optical properties, stability-range and other characters of tridymite.

The fringe-structure of the tridymite at Bundeena and Pymble is exactly matched by the examples figured by Flett (1911) and Reynolds (1908).

Reflecting on the occurrence of tridymite in general one can stress that this mineral develops under two very differing environments: (*a*) that in which quickly elevated temperatures affect felspathic sandstones adjacent to basic intrusions; and (*b*) that in which late magmatic fluids, acting upon rhyolitic and trachytic lavas, bring about the eventual crystallization of tridymite plates, often in cavities.

It is thought by the author that this is the first record of tridymite in New South Wales, and it is proposed to make further field and petrological study of some of the contact-metamorphosed aureoles in the Hawkesbury Sandstone of the Sydney Basin. In a later communication fuller details and illustrations of the occurrence of tridymite will be given.

ACKNOWLEDGEMENTS.

Acknowledgement is here made of financial help from the Commonwealth Research Grant.

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THE STRATIGRAPHY AND GENERAL FORM OF THE TIMOR ANTICLINE, N.S.W.

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CONTENTS.

INTRODUCTION AND GENERAL PHYSIOGRAPHY.

The Timor Anticline is developed in a belt of Devonian rocks in the Upper Isis River district about 16 miles north-east of Murrurundi, which is distant 218 miles by rail from Sydney.

It occupies the lower country south of the Liverpool Ranges, and the portion here described is the core of the fold as developed north of Timor Estate in the Parishes of Crawney and Lincoln, County Brisbane.

The Devonian belt here is a continuation of the Devonian rocks which lie to the south and south-west of Tamworth and Nundle, and which were described many years ago by Benson (1913–1918) in his Serpentine Belt series of publications.

The anticlinal structure is the southward continuation of a geanticline known to trend from west of Bingara and Barraba, through Manilla, and southward to west of Tamworth and Nundle. In the country south-west of Tamworth, this anticlinal zone is succeeded westerly by the Werrie Basin, described by Carey (1934).

The general physiography of the area may be summarized as follows :

The Isis River in the Timor district is in a late mature development, and to the north its headwater tract merges into rugged country of the foothills on the Liverpool Ranges, which shut in the valleys to the N.W., N and N.E.

The valley-floor, which, in the region described, is from 2,100–2,400 feet above sea-level, is not heavily alluviated ; however, notable aggradation of the river is seen further south between Timor and Waverley.

Between the present level of the alluvial plain and the high country of the Liverpool Ranges is a number of erosion levels which can easily be traced in the field. One of these is the old sub-basaltic surface which lies at an average elevation of about 2,700–2,800 feet above sea level. On this surface were poured the Oligocene lavas. Surmounting the basaltic ridges are several peaks the highest and most spectacular of which is Wombramurra Peak (4,100 feet). These eminences alternate with gaps or passes, of which Crawney Pass (3,650) is the best known.

Since full physiographic details are not required in the present discussion, it is sufficient to note that pulsatory uplift of a basalt-covered peneplain led to the development of valley-in-valley topography, at least one erosion level being for the most part a revealed peneplain surface. Modifying the simple plan of valley-in-valley sculpture is the work of numerous subsequent tributaries of the Isis River. Remarkable adjustment between the detailed physiographic evolution and the geological structure is manifest everywhere in the area.

PREVIOUS WORK AND SCOPE OF THE PRESENT PAPER.

Practically no stratigraphical or structural investigation has been made upon the area. Carne and Jones, in describing the limestone (1919), drew attention to the presence of an anticlinal structure. Earlier references to the district are to be found in the record of fossils collected by Cullen (see Dun, 1900) and the description of *Endophyllum schlueteri* by Etheridge (1898). A cryptic reference by Phillips (1875) no doubt refers to the Crawney limestone in County Parry. Benson (1918, 1922) gave lists of fossils from the Isis district and from the large deposit of limestone on Wombramurra Creek, north of the Liverpool Ranges, which may be the continuation of the Isis belt. A study of the Wombramurra outcrop is most desirable.

The first-named author of the present paper determined the existence of the anticline independently, and intermittently over several years mapped the area, in great detail, completing the field work in 1942. In 1945 he supervized further detailed investigation and check-mapping by the other authors. The results of the work are embodied in the map (Plate XXII), which is intended to show the salient structure.

The present paper deals with the general stratigraphy and summarizes the morphological features of the anticline. The stratigraphy has been dealt with only as an aid to the structural studies.

The genetic aspect of the structural features contributes to a study of tectonic evolution of the Hunter-Manning Province now being completed by Osborne.

STRATIGRAPHY.

Rocks of Middle and Upper Devonian age are exposed in the valley of the Isis and its tributaries. The higher ground is given over to basalt flows with occasional plugs, sills and small sills of dolerite; these are all of mid-Tertiary age.

The chief feature of the stratigraphy is the existence of a large mass of limestone, richly fossiliferous in corals, brachiopods and hydrozoans. This limestone (here named the Timor Limestone) is to be correlated with part of the Moore Creek sequence of the Tamworth and Attunga districts, which has been fully investigated by Brown (1942). We are indebted to Dr. Brown for having checked the fossil-horizons of the Timor Limestone.

The limestone is underlain by tuffs, conglomerates, banded cherty-claystones with slump bedding and intraformational brecciation, thin spilite flows and breccias, and thin dolerite sills. Many of the fragmental rocks are fairly high in soda content. The rocks overlying the limestone comprise tuffs, conglomerates and banded tuff-claystone units.

It is clear from geographic and structural relationships between the Timor area and the Serpentine Belt province to the north that the rocks of the anticline are definitely the equivalents of portions of the Tamworth and Barraba successions, including probably the Baldwin Agglomerates (which form the lower portion of the Upper Devonian sequence).

The limestones vary in thickness, but reach a maximum of 760 feet in the neighbourhood of "Allston" Station. Much of the surface of the country within the central part of the anticline is given over to limestone or to subordinate calcareous shaley beds so that the map displays a wide core of limestone (Plate XXII).

In mapping the main fold and also the smaller structures (see below), considerable help was afforded by the zonal character of the limestone succession. Distinct fossil zones were noted (more from the presence of one or two prominent genera than from any marked zonal assemblage), and the recognition of these zones helped greatly in delineating the structural detail in complicated areas. This was especially true of the Glen Dhu complex.

The persistence of a rhythmically banded shale-limestone zone at the base of the main mass, and of a cherty silicified and cavernous zone at the top of the mass, further expedited the structural mapping. In effect, various fossiliferous zones became reliable tectonic indicators in areas of faulting.

It is proposed to state the generalized sequence of the area with special reference to the limestone.

Descending stratigraphically, we have:

	Maximum Thickness in Feet.
Barraba Series—	
Mudstones with bands of fine grained tuff and frequent *Lepidodendron Australe* and *L. Osbornei*. Occasional layers with *Radiolaria*	300
Fine tuffs with angular and rounded pebbles in acid matrix (Baldwin Agglomerate type)	50
Tamworth Series—	
Banded tuff-chert material	100
Fine claystones	200
Well bedded tuff-chert material	250
Tuff-chert layers with intrusive tuff	80
Coarse albitic breccia	100
Blue fine tuff	80
Conglomerate abruptly changing in texture	150
Blue tuff and coarse breccia	80
Blue-green keratophyric tuff	120
Tuffaceous chert with *L. Australe*	180
Tuffs with some intraformational complications	90
Evenly bedded mudstones with *L. Australe*	80

The Timor Limestone—

Siliceous, sometimes agatized, cavernous limestone: 90 ft.

Horizon 8. Glen Dhu zone of corals including *Tryplasma*: 120 ft. from top.

Horizon 7. *Endophyllum* zone: 175 ft. from top.

Horizon 6. *Pachypora* abundant: 225 ft. from top.

Horizon 5. Gastropods abundant: 280 ft. from top.

Horizon 4. *Amphiphora*, *Favosites* and rugose corals abundant: 300 ft. from top.

Horizon 3. Stromatoporoids abundant (Allston Zone): 550 ft. from top.

Horizon 2. *Heliolites* Zone: 570 ft. from top.	
Horizon 1. Brachiopods (including rhynconellids) abundant: 590 ft. from top.	
Blue limestone: 90 ft.	
Rhythmically banded shale-limestone with characteristic dark-red or black soil (Trilobite recorded at base): 80 ft.	
Total limestone	760
Chert-tuff strata with intraformational disturbances (Tamworth facies)	50
Tuffs and cherty-claystones	145
Tuffs with alternating coarse and fine grain	150
Well-bedded blue-green cherts	40
Agglomerate with spilitic and limestone fragments ..	10
Chert-claystone and shale-breccia	135
Green keratophyric tuffs with quartz veins	50
Claystones (Tamworth type)	20
Tuffs and claystones	100
Blue-green tuffs and albitic tuff	35
Spilite	10
Hard resistant tuff bar	10
Blue cherts	60
Spilite flow	15
Cherts and tuffs (with some silicification)	245
Well-bedded tuff	20
Breccias alternating with fine tuff, containing *crinoid.*	
Hard blue tuffs with cherty fragments	25
Shaley mudstones 20 ft. exposed. (Base of the Tamworth Series not encountered)	20
Total of section	3,760

Regional Distribution.

The limestones are confined to an area, partly rectangular, of approximately seven square miles. The general trend of this area, which is three miles wide, is N. 20° W., this being the main direction of strike of the rocks. A little to the south of Isaacs Creek the southernmost tip of the anticline is seen in portion 65 (Parish of Crawney), but soon the outcrop widens and swells northward and eastward into the heart of the fold. This broad development of limestone continues several miles to the valley of Dead Eye Creek, where thrusts cut across its northern margin.

From portion 78, Parish of Lincoln, to the north only a narrow outcrop of limestone is present. This runs parallel to the Isis River and parallel to the Crawney Road, and here has a steep dip (48°) to the west. Eventually this narrow belt dies out just north of the parish boundary (Crawney-Lincoln) near Oakey Creek.

Lying east of the main outcrop, at its southern end, is an isolated sector of limestone. This is well-exposed in the country immediately north and south of the headwaters of Isaacs Creek. Faults separate it from the main anticlinal limb.

On the west side of the Isis from Glen Dhu to a little south of Isaacs Creek, the structure is continuous, possessing a dip varying from 15–20° in the direction W. 20° S. Fairly constant strike is maintained, as also is the thickness, viz. 760 feet. The limestone has markedly determined the physiographic conformation in this locality.

Small outcrops of limestone, especially of the coralline Glen Dhu zone, are found in the valley of Dead Eye Creek, and considerable faulting and structural complexity are responsible for the general distribution here.

The rocks of the Tamworth Series which underlie the limestone are not exposed sufficiently to permit satisfactory study. They are found in creeks in the central part of the area, especially along the axis of the anticline, e.g. in Perry's Creek.

The Tamworth Series, which succeeds the Timor limestone, is best studied in the eastern portion of Isaacs Creek and south therefrom in Branch and Double Creeks. In these latter streams one notes the large development of albitic tuff and considerable amounts of the characteristic tuff-chert sediment with contemporaneous disturbances.

The Barraba mudstones and the limited Baldwin Agglomerate are found flanking the limestone on both sides, and succeeding it southward in the direction of plunge.

The fact that there is a much greater development of Tamworth strata in the southerly pitching nose-area of the anticline, as compared with the flanks of the structure, suggests that some erosion of the supra-limestone strata took place before the Upper Devonian sediments were deposited. The important implication of these data is briefly treated within the next section.

STRUCTURE.

Relations of the Tamworth and Barraba Series.

This matter has been carefully examined in the field. In one place in Upper Isaacs Creek a slight angular unconformity is demonstrable, by noting the dip and strike relationships. Elsewhere in the country between Branch Creek and to the N.W. and N.E. the Barraba Series transgresses the *Tamworth* Series only very slightly. The fact that the anticline is plunging makes difficult the investigation of problems relating to structure. A point bearing on the question, however, is that of the evidence of compaction and diagenesis ; in the Tamworth Series physical processes have developed to a much greater degree than in the Barraba rocks. Further, the latter are free from quartz veins which are found in the former. This suggests a lapse of considerable time between the periods of sedimentation. Yet again is the testimony of minor structures in the Tamworth Series which imply the operation of stresses prior to Barraba deposition.

Therefore it seems justifiable to assume a time-break between the two series, and to postulate the progress of some crustal warping with attendant contemporaneous erosion in this area.

The Timor Anticline.

This structure is best designated an anticline although in point of fact the limestone outcrop almost completely closes so as to produce a dome-like unit. The closure on the north is due to thrusting which has bent down the axial zone of the anticline and delimited the central structure in that direction.

The fold is seven miles long and approximately three miles wide. The general strike is N. 20° W., but some swinging of the whole arch is clearly detectable. The axis of the fold, as plotted in many cross sections, bears out the swing (see map).

The anticline is essentially a flat-topped arch with marginal dips of 25–28° on the west, and to the east a maximum of 51°. Its cross-section is simple in the broad sense, but many interesting minor features occur, which have important structural significance. The minor tectonics of the area are admirably displayed for demonstration.

Chief amongst the minor structures (most of which will be genetically discussed in another paper) are:

(*a*) A trough-faulted rift cutting obliquely across the main axis. This is developed N.E. and S.W. of Perry's Creek. Tensional fractures prominent here.

(*b*) A stair-case-like cross fault system developed athwart the central part of the rift.

(*c*) Several sharp synclinal crumplings, and two miniature anticlinal crumplings of great sinuosity. Also a number of thrust (quasi-imbricate) zones with combinations of both plastic deformation and shattering.

(*d*) On the south-plunging nose of the fold are several minor contortions (seen well about the lower Isaacs Creek area.) These imply the structural weakness of the limestone when heated by the effects of severe deformation.

Some further details may now be given concerning the structures of (*a*) and (*b*), although more will be said in a later communication.

The rift breaks obliquely across the crestal zone of the region, and is more or less meridional in its trend. It has torn the limestone open by the operation or two longitudinal tensional faults, and differential block-faulting has occurred within the zones bounded by these fractures. The limestone, in several of these minor block-units within the trough, has been displaced through considerable relative vertical distances, e.g. up to 100 feet. The trough-fault in Perry's Creek lies in this category, since a little to the south of the creek the first ridge is capped by a restricted area of basal beds of the limestone. This small outcrop represents the continuation of the Perry's fault-trough, the vertical displacement being much less than that recorded in Perry's Creek. Further, in the case of the cap we find that the limestone in contact with the bounding faults has been rotated by the frictional drag, producing a saucer-shaped structure in limestone. This same trough extends in a northerly direction and an examination of the structures in the area indicates a differential movement of blocks within the zone of fracture.

Faults other than Minor Examples.

The faults which are present may readily be classified into:

(*a*) Tensional faults of the valley floor and of the eastern margin of the anticline.

(*b*) Parallel thrusts of the Glen Dhu complex.

(*a*) These comprise three meridional fractures: one trending along the line now occupied by the river, and the other two forming a senkungsfield in the eastern Isaacs Creek sector.

The meridional fault (to be called the Isis Fault) begins in the north at the junction of Perry's Creek and the Isis River, and strikes approximately S. 30° E., increasing in downthrow southward.

This predetermined line of weakness has not always been the site of the river bed, for studies of the physiographic evolution make it clear that the river originally occupied a subsidiary anticline (now east of the Isis) and in course of its development migrated westerly along the limb of the anticline into the fault-zone where it has entrenched itself to some degree. The fault has given rise to marmorization of the limestone near the road-bridge over the river, about one mile north of Isaacs Creek.

The trough on the eastern side of the area is complicated by the existence of small cross faults within the walls of the senkungsfeld. There are some steep dips and corrugations in the beds adjacent to the faults, while within the trough an exotic band of limestone indicates by its differential movement and variable positions that considerable complexity has marked the movement of the blocks.

It would appear that the tensional structures so far described, developed during periods of stress-relief associated with and following the main deformation which produced the anticline.

(*b*) The full account of the thrusts and associated features at Glen Dhu are reserved for genetic discussion in the work now being produced by one of us (G.D.O.). It will be sufficient to summarize the structural development here by saying that succeeding the main folding which produced the geanticline between Bingara (in the north) and Dungog (in the south) there was superimposed a system of forces, chiefly related to a southward or south-eastward thrusting and some rotational stresses. These brought about the development of faults trending N.N.E. and S.S.W. This north-north-west stress caused some flexuring of the axial zone of the anticline, thus shortening the fold in the crestal direction.

AGE OF THE STRUCTURES.

From correlation of the Isis area with other areas whose geological history is fully known we are of the decided opinion that all of the deformation took place in the Hunter-Bowen diastrophic cycle. The Timor Anticline suffered some special stress conditions within that diastrophism, and received its closure then.

SUMMARY.

In the foregoing pages an account is given of the Timor Anticline, stress being laid on the structural features. It is shown that the Isis River district occupies an important place in the tectonics associated with the gradual unfolding of the Upper Palæozoic formation. The stratigraphy has been dealt with fairly fully, and zone fossils are listed for the Timor limestone, which forms the basis of the tectonic study, being, as it is, the main datum for all structural investigations in the area described.

ACKNOWLEDGEMENTS.

The authors are anxious to place on record their appreciation of the splendid hospitality and keen interest in their work shown by Mr. and Mrs. George Ivin and family, of " Allston ". We would also record our indebtedness to Mr. C. J. Ivin, of Murrurundi, who by his local geological knowledge has saved us much time in our work. One of us (G.D.O.) acknowledges the financial assistance provided by the Commonwealth Research Grant of the University.

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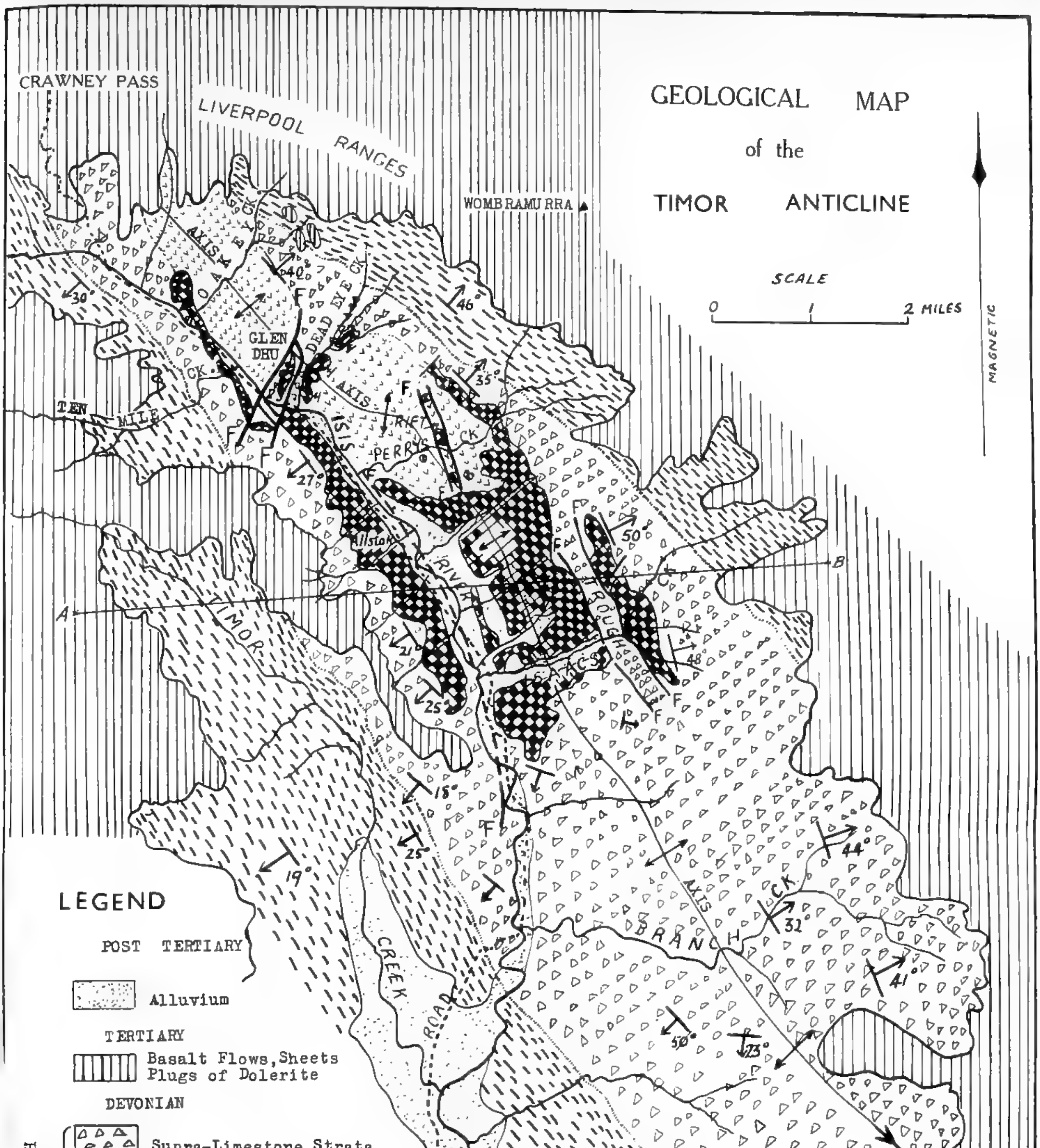

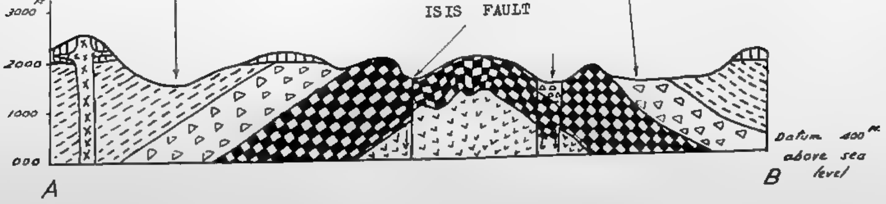

Section along Line A—B.

THE GEOLOGY OF THE CANOWINDRA DISTRICT, N.S.W.

PART I. THE STRATIGRAPHY AND STRUCTURE OF THE CARGO-TOOGONG DISTRICT.

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With Plate XXI and two text-figures.

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CONTENTS.

I. INTRODUCTION.

The district geologically mapped and described in this paper lies to the north of Canowindra and to the south-west of Orange. Cargo and Toogong are the chief localities within the area, and are both about 200 miles from Sydney by road.

The area studied is of approximately 330 square miles; bounded to the west by the Mandagery Range and Nangar Mountains, and to the east by the Black Rock Range.

Towards the close of the last century extensive gold-mining operations were carried out at Cargo and Burdett. Brief accounts of the geology of the Cargo goldfield have been given by Hutton (1875), Wilkinson (1878) and Anderson (1890). In 1915, Andrews and Morrison carried out a geological survey of the immediate vicinity of Cargo, their purpose being to revive interest in this mining field.

Limestones near Cargo and Cudal have been reported upon by Carne and Jones (1919), and some of the outcrops are shown on their maps.

The geology of the country adjoining the north-west section of this area has been described by Joplin and Culey (1937); and Sussmilch (1906) has noted the stratigraphy of the Silurian and Devonian rocks in the parish of Barton, adjoining the north-east section of the district.

II. Physiography.

Taken as a unit, the district is undulating to hilly, showing a stage of late maturity in the erosion cycle. The elevation above sea level varies from that of the Orange-Blue Mountain plateau (3,000 feet) to the level of the Lachlan-Belubula valley (1,000 feet).

Along the eastern and western sides of the area examined are prominent quartzite ridges with meridional trend, rising 600 to 1,000 feet above the surrounding country, which is undulating, with a general slope from the north-east (near Mt. Canobolas) to the west and south.

The gradual slope is interrupted by a low, east-west watershed, extending from Columbine Mountain to Burdett. To the north, the district is dissected by the Mandagery-Boree drainage system, while to the south, streams enter the Belubula River, either separately or by way of Canomodine Creek. Both Mandagery Creek and the Belubula River flow into the Lachlan River, but follow widely different courses.

The main streams of the Mandagery-Boree drainage system rise in the Lachlan-Macquarie divide and in the Canobolas Mountains, and flow in a south or south-westerly direction towards Toogong. The creeks follow meandering courses, for the most part between banks of alluvial deposits 12 to 20 feet high.

South of Cudal, flows of Tertiary basalt follow the valleys of the present-day streams, preserving old alluvial deposits. The streams have been rejuvenated, cutting steep-sided gorges up to 50 feet deep through the basalt.

A few miles south-west of Toogong, Mandagery Creek loses its aspect of late maturity as it leaves the gently undulating country and flows through a gap in the resistant quartzites of the Mandagery Range.

Most of the creeks on the south side of the east-west watershed join either Nyrang or Canomodine Creeks. These become progressively more youthful towards the east, depending mainly on an increasing gradient in this direction. Canomodine and Four Mile Creeks rise near Mt. Canobolas and flow in a southerly direction to enter the Belubula River. Like Mandagery Creek, they have cut deep gorges through the quartzites, but their average gradient is steeper. They are not associated with large areas of gravels, and are relatively youthful compared with Mandagery or Boree Creeks.

The undulating country between the bordering quartzite ranges consists mainly of slates, lavas, pyroclastic rocks and limestones, invaded by porphyry and partly covered by basalt flows.

Certain of these rock types are much more resistant to erosion than others, and give rise to prominent ridges which parallel the strike of the beds (e.g. the phyllites west of Mandagery Creek, the coarse tuffs and breccias west of Cudal, and the crystal tuffs south of Cargo). Between Burdett and Barragan, the rock types are mainly porphyry and slate. The slates are more resistant and form long, parallel ridges ; the valleys between the slate ridges are broad and mature.

The courses the streams follow are dependent partly on rock type and partly on directions of jointing and faulting. Canomodine Creek and one of its tributaries flow along fault zones on either side of Columbine Mountain, and the former creek also follows the strike of a fault near Canomodine Station. The alluvium of Oaky and Boree Creeks conceals a fault near Toogong.

Several of the creeks follow the strike of the beds for some part of their length, notably Mandagery, Four Mile, Cargo and The Grove Creeks. Jointing is largely responsible for the minor deviations in the stream courses.

At Gum Flat, near Cargo, there is an exceptional thickness of Tertiary or Pleistocene sediments, covered by Recent alluvium. Shafts indicate a maximum thickness of 370 feet of clays and gravels. Boulders of Upper Devonian quartzite occur in the deeper levels, but this rock does not outcrop in the present restricted catchment and must have been derived from the quartzite ridges to the east. Consideration of the levels of the base of the Gum Flat sediments as revealed by mine shafts and surface boundaries shows that the slope of the old valley floor is from south-east to north-west, consequently it is probable that there has been a reversal of drainage. The old stream had its source in the quartzites south-east of Cargo, flowed west across the low divide between Canomodine and Cargo Creeks, then north-east past Gum Flat, to join Cargo Gully and Gerybong Creek.

At a later stage, due probably to local subsidence, prolonged alluviation took place. The lower part of the present Canomodine Creek then began to cut back in a northerly direction and capture the headwaters of the old Gum Flat stream. It seems likely, therefore, that the headwater tract of Canomodine Creek originally emptied into Gerybong Creek, by way of Gum Flat.

Evidence of the former course of an old stream lies in the occurrence of a patch of large, water-worn boulders high up on the eastern side of the valley of Canomodine Creek, south-east of Cargo.

As a result of the river capture noted above, and the consequent reversal of drainage, a watershed was set up in the alluvium of Gum Flat, west of Cargo, and the creeks assumed their present directions of flow.

III. Stratigraphy.

The greater part of the stratified and effusive rocks belong to the Older and Middle Palæozoic era; a minor part of the area is covered by Tertiary lavas and Cainozoic alluvial deposits.

(1) *Ordovician.*

The oldest rocks outcropping in the district are of Upper Ordovician age. They are black, banded slates and cherts, with well-marked laminæ which show differential weathering, giving a distinctive appearance. The rocks occur in two small inliers bounded by faults, three miles east of Cargo. They are highly folded, with approximate meridional strike.

Their Upper Ordovician age has been established by the finding of the following graptolite fossils in portion 98, Parish of Cargo:

Diplograptus cf. *truncatus.*
,, cf. *rugosus* var. *apiculatus.*
,, cf. *quadrimucronatus.*
Cf. *Retiograptus* sp.
Dicellograptus sp. (perhaps allied to *D. pumilus*).
Cf. *Lasiograptus harknessi* var. *costatus.*

These graptolites have been determined by Mrs. K. Sherrard, M.Sc.

(2) *Silurian.*

Strata of this age occupy the greater part of the area mapped. The sequence varies somewhat over such a large district, but a generalized succession is shown in Table I, where it is correlated with that of the Molong-Manildra (Joplin and Culey, 1937) and Wellington (Basnett and Colditz, 1945) districts.

(i) *The Lower Sedimentary Series.* Rocks which appear to underlie the Cargo Andesitic Series (and thus to belong to a horizon equivalent to the Lower Sedimentary Series of the Wellington district), occur six miles south-east of Cargo. They are bounded on the east by a fault junction with Upper Devonian quartzites, and appear to dip under the andesites to the west.

The rocks are blue-grey and reddish slates, passing upwards into beds of slates and fine tuffs. These are overlain by a limestone, the topmost bed of the series.

(ii) *The Cargo Andesitic Series.* The members of this series outcrop in two belts belonging to the same series and repeated by folding. The larger area exposed is in the Cargo district, where the series is four miles wide, due however, to complicated folding and faulting. The smaller belt extends almost north-south, through Barragan, to the west of Cargo.

The series consists of a great variety of andesites, trachyandesites, basalts, tuffs and breccias, with interbedded clay slates, cherts and occasional limestones.

TABLE I.

Correlation of Silurian Stratigraphy.

Cargo-Toogong.	Molong-Manildra.	Wellington.
7. Rhyolites.	5. Rhyolites.	
6. Slates.		
5. Canomodine limestone.		
4. Slates and tuffs.	4. Manildra beds.	3. Upper Sedimentary Series.
3. Cargo Creek limestone.	3. Molong beds.	
2. Cargo Andesitic Series.	2. Andesites.	2. Volcanic Series.
1. (?) Lower Sedimentary Series.	1. Limestone (Molong).	1. Lower Sedimentary Series.

It has been found inadvisable to map individual flows, slate or tuff beds within the series, because of their narrow surface outcrop and lateral variation. North and north-east of Cargo, mapping is hindered by soil cover, but good exposures occur in the country to the south-east, which has been dissected by Canomodine Creek and its tributaries.

A composite sequence, deduced from these exposures, is as follows :

(Cargo Creek limestone).
10. Tuffs.
9. Augite hornblende andesite.
8. Breccias, tuffs, cherts.
7. Amygdaloidal basalt.
6. Porphyritic trachyandesite (with large amygdules).
5. Augite andesite.
4. Trachyandesite or keratophyre.
3. Thin limestone bed.
2. Breccias, and andesites with xenoliths.
1. Cherts and slates.

All of these beds are discontinuous and the complete sequence will not be found in any one section.

The cherts and slates which appear to be the oldest strata outcrop in an anticlinal crest on Canomodine Creek and may belong to the Lower Sedimentary Series. Overlying these are dark grey-green breccias, and andesites containing rounded xenoliths like those near Wellington (Colditz, 1947). In places, a thin limestone bed follows ; usually devoid of fossils and somewhat marmorized.

The trachyandesites or keratophyres next in the sequence do not occur in the Canomodine Creek succession, but outcrop nearer Cargo. They are light grey, amygdaloidal rocks with small felspar phenocrysts in a holocrystalline base. New Chum Hill (west of Cargo township) is composed of this rock, and a similar type outcrops north and south-east of this locality. To the north, the keratophyres have been metasomatized by iron-bearing solutions, and appear as black, fine-grained amygdaloidal rocks.

On Canomodine Creek and to the south, the next horizon is that of a greenish andesite with pink felspar phenocrysts. Aggregates of calcite seen under the microscope indicate the former presence of augite.

Towards the eastern side of the Andesitic Series on Canomodine Creek, porphyritic trachyandesites outcrop, followed by a fairly persistent band of coarse breccias. The stratigraphical position of these rocks is a little uncertain, as they are separated from the preceding strata by a fault, and do not occur on the south-western side of the series.

The trachyandesites vary slightly, but most are characterized by large phenocrysts of pink or cream plagioclase. In some localities they are markedly amygdaloidal, the calcite amygdules attaining a diameter of 35 millimetres.

The breccias are generally coarse, grey-green rocks, containing large angular fragments of andesites and cherts. They are well-stratified, and near the top of the sequence are interbedded with cherts and reddish clay shales. The latter underlie a limestone which will be taken as the equivalent of the Cargo Creek limestone, the bed which marks the top of the Andesitic Series. Breccias similar to those noted above are widespread around Cargo, especially in Copper Gully.

Along Canomodine Creek, on the south-west side of the Andesitic Series, the sequence is different. The augite andesite (5) is interbedded with tuffs and overlain by a thin flow of amygdaloidal basalt. An andesitic breccia with a matrix of calcite follows, and is possibly equivalent to some of the breccias which overlie the porphyritic trachyandesites. The topmost lava in this locality is an augite hornblende andesite with phenocrysts of tabular plagioclase closely packed together.

Most of the area north and east of Cargo is occupied by an andesitic lava with phenocrysts of cream plagioclase and occasional augite in a fine-grained black groundmass. The phenocrysts usually have a glomeroporphyritic arrangement, and the base is mainly of felspar and magnetite needles showing a variolitic structure. It is not clear whether this rock has suffered metasomatism or devitrification. A similar type from the Wellington district has been described (Colditz, 1947) as a devitrified glassy augite andesite. It occurs at the base of the Volcanic Series, which is in keeping with the position of this rock in the Cargo district.

It may also be pointed out here that the succession in the volcanic series of Cargo and Wellington shows other similarities, such as the presence of augite hornblende andesite and volcanic agglomerate near the top of the series.

Approximately parallel to, and four miles west of, the Cargo Andesitic Series, is an equivalent series, occupying the core of an anticline. The northern extension is terminated by a fault; the beds continue south for seven miles, and then plunge beneath overlying tuffs and slates.

The series has not been exposed to as great a depth as that of Cargo, so that only the uppermost beds outcrop. The oldest of these rocks occur in the centre of the fold near the northern end. They are dark, grey-green augite hornblende andesites resembling those near the top of the Cargo Series. These are overlain by coarse andesitic breccias, which consist of sub-angular fragments of augite andesites, cherts, etc., in a tuffaceous matrix rich in calcite, some of which is stained pink.

(iii) *The Cargo Creek Limestone.* This bed directly overlies the Cargo Andesitic Series, and is best developed along Cargo Creek three miles south of Cargo, where it outcrops continuously for four miles, with an apparent maximum thickness of 3,000 feet. Strike faulting, however, may have increased the width of outcrop.

The limestone is massive, with few shaley beds, and fossils are not abundant. *Favosites*, *Heliolites*, *Tryplasma* and *Pentamerids* (probably *Conchidium knightii*) have been found.

North-west of Cargo several small limestone lenses outcrop, separated from the Andesitic Series by tuffs, cherts and slates. They contain *Halysites*, gastropoda and bryozoa. These limestones are probably of the same horizon as the Cargo Creek belt. In the south, continuous formation of limestone took place, while further north volcanic and marine conditions predominated.

The limestones near the Canangles Road, three miles south-east of Cargo, seem to be equivalent to the Cargo Creek belt. North of the road the limestone occurs in a syncline, plunging to the north-west; its north-westerly extension being terminated by a fault. South of the road the limestone again outcrops, having the structure of a south-plunging syncline, but the eastern limb of the fold is cut off by a fault, bringing the limestone in contact with Upper Devonian rocks.

These limestones are somewhat more fossiliferous than the main belt. The basal beds on the west side of the northerly-plunging fold contain small Rhynchonellids, while on the eastern side a brachiopod resembling *Stropheodonta* is present in a reddish-coloured marble. Higher up in the limestone *Heliolites*, *Tryplasma*, Pentamerids, Stromatoporoids and (?) *Favistella* have been found.

Near Barragan, limestone of the same horizon overlies the Andesitic Series, but is not well developed, occurring in isolated lenticular beds, mainly along the eastern margin of the breccias.

North of the Oaky Creek fault and north-west of Cudal, the limestones do not directly overlie the Andesitic Series, but are probably of the same horizon. Here the andesites would again occur in the core of an anticlinal fold, but have not yet been exposed by erosion. In these limestones *Favosites*, *Tryplasma*, *Halysites*, *Pachypora*, Pentamerids and bryozoa have been found.

(iv) *Tuffs and Slates.* South of Cargo a series of crystal tuffs with interbedded cherts and slates overlies the limestone of the Cargo Creek belt.

The crystal tuffs are best developed in the southern parts of the area, notably between Cargo Creek and the Belubula River and east of Lockwood. These two occurrences are equivalent; situated on the east and west sides, respectively, of a syncline. Proceeding north along the strike of the beds, the tuffs become finer in grain-size and pass into cherts and clayslates.

The tuffs on the north-west side of Cargo Creek are dark, fine-grained rocks, some resembling basalt in hand specimen, others showing spheroidal weathering or traces of bedding. Under the microscope, crystals of plagioclase, quartz, orthoclase, augite and brown hornblende are seen.

Towards the upper part of the series, slates predominate over tuffs, except between Canomodine and the Belubula River, where coarser tuffs are interbedded with the slates.

The maximum thickness of this series of tuffs and slates is about 5,000 feet.

In the Cudal district the equivalents of the Cargo Creek limestone are overlain by slates, then by pyroclastic rocks ranging from cherts to coarse breccias. These, together with the overlying slates, make up the "Manildra beds" of Joplin and Culey (1937), the slates and limestones being grouped together as the "Molong beds". The pyroclastic rocks may be correlated with the crystal tuffs south of Cargo. The breccias are best developed near Manildra, but thin out to the south, passing into tuffs, cherts and clayslates.

Two thin limestone beds occur in this pyroclastic series north-west of Cudal, and in portion 52, Parish of Cudal, fossiliferous limestone overlies a breccia which is also rich in fossils. *Favosites*, *Heliolites*, *Tryplasma*, *Syringopora* *Mictocystis*, *Orthosina* (?), Stromatoporoids, crinoid stems and bryozoa are present. In addition, *Dalmanites* and *Mucophyllum* have been previously recorded from this locality (Joplin and Culey, 1937).

This horizon is traceable to the south through "Derowie" (east of Toogong) to the cross-roads three miles south-west of Barragan. Small lenticular patches of limestone outcrop at these places, and near "Derowie" a compact crystal tuff is interbedded with slates which overlie the limestone. *Halysites* and *Favosites* are present in the limestones.

(v) *The Canomodine Limestone.* This thick mass of limestone appears to overlie the tuffs and slates four miles south of Cargo. The belt has a maximum width of outcrop of two miles, due to folding in a synclinal structure.

On the western boundary, in the vicinity of Barrijin Trigonometrical Station, the limestone dips off a lenticular mass of andesites, andesitic breccias and tuffs. These beds do not appear on the eastern side of the syncline.

The Canomodine limestone is very massive and relatively unfossiliferous, resembling the Cargo Creek limestone. Carne and Jones (1919) infer that these limestones are of the same horizon, but examination of the area between these beds shows that the two limestones and the intervening beds (tuffs and slates) dip in the same direction (south-west), so that the Canomodine limestone is stratigraphically above the Cargo Creek bed, unless a major strike fault be postulated at the junction of the slates with the Canomodine limestone. No evidence of such a fault has been found, however.

The Canomodine limestone thins out rapidly to the north of Barrijin Trigonometrical Station, but an isolated outcrop in portion 176, Parish of Toogong, north of the Nanami Lane, is possibly of this horizon. There, the limestone has been partly silicified and jasperized ; it contains abundant fossils, including *Halysites*, *Favosites*, *Heliolites*, *Tryplasma*, *Mucophyllum*, Stromatoporoids and bryozoa.

The limestone previously described as occurring interbedded with the breccias west of Cudal may be of this horizon.

(vi) *Slates.* Slates which overlie the Canomodine limestone outcrop in the synclinal structure between Avenel and Barragan, and those overlying the " Manildra " breccias may be noted here. At the last-named locality, some of the slates occur in an extensive shear-zone, and have been converted to phyllites. These rocks are traceable south along the boundary of the Upper Devonian strata as far as Burdett, where they are surrounded by porphyry.

(vii) *Rhyolites.* Rhyolitic lavas overlie the slates and phyllites and underlie Upper Devonian quartzites six miles west of Cudal. The lavas become more extensive to the north near Meranburn, where they have been noted by Joplin and Culey (1937). To the south they thin out and disappear two miles south of Dulladerry Creek, but an isolated outcrop occurs at Burdett.

The basal flows are white and purple rhyolites, with small phenocrysts of quartz and felspar in a felsitic groundmass. Succeeding lavas are mainly banded rhyolites ; some spherulitic types are interbedded.

The banded rhyolites show excellent flow structure with local contortions ; the colour varies from pink to pale green, with purple bands. Phenocrysts of quartz and altered felspar are present.

The lavas show evidence of silicification, and some mineralization, as phenocrysts are often replaced by quartz, and less commonly by pyrites, which has mostly been altered to hæmatite.

The age of these lavas is thought to be Upper Silurian, as a spherulitic rhyolite is interbedded with the slates which underlie the main lava flows. These slates do not resemble the typical Garra (Lower or Middle Devonian) beds, and are probably Upper Silurian.

Sussmilch (1906) has described rhyolitic lavas from the Parish of Barton (on the Cargo-Orange road), and places them at the top of the Silurian sequence.

(3) *Upper Devonian.*

Rocks of Upper Devonian age occur as long, meridional-trending belts on the eastern and western sides of the district, lying about 15 miles apart. They may be divided into an Upper and a Lower Series.

The Lower Series has restricted distribution, occurring in an anticlinal structure north of the Black Mountain (Fig. 2). It consists mainly of chocolate and green shales and mudstones. On Paling Yard Creek, a variety of *Lepidodendron* has been found in a green tuffaceous mudstone.

The Upper Series is well developed on both sides of the district. The main rock types are quartzites and sandstones, with some interbedded grits and red shales. These rocks make up the rugged country of the Mandagery Range and Nangar Mountains to the west, and the Columbine and Black Mountains, and the Black Rock Range on the east.

The quartzites vary from white to yellow or brown, and have resulted from silicification of arenaceous sediments during folding. Ripple marks, current bedding and worm burrows are present, indicating shallow-water deposition, but no fossils have yet been found in the district mapped. However, Sussmilch (1906) noted the occurrence of *Rhynchonella pleurodon* and *Spirifer disjuncta* on Spring Creek, eight miles north-east of Cargo.

The red colour of the shales changes to green along joints and watercourses, due to the leaching of iron compounds. In the gorge of Canangle Creek and further south, an impure limestone occurs in thin bands in the quartzite series.

The quartzites are overlain by red shales, followed by conglomerates. The latter have been mapped together with rocks of Lower Carboniferous age, and will be described below.

(4) *Lower Carboniferous.*

Rocks of definite Carboniferous age outcrop east of Columbine Mountain. They are greenish mudstones grading into tuffs of fine to medium grain-size. They contain abundant plant stems and at least two species of *Rhacopteris.*

The better-preserved species is allied to *R. petiolata*, a fern which occurs at the top of the Tournaisian in Great Britain, equivalent to the top of the Lower Kuttung of N.S.W. The other species is more like *R. inequilatera.*

The Carboniferous sediments appear to rest conformably on the Upper Devonian strata, and in the absence of a structural break the boundary should be placed at the base of the conglomerate noted above.

If this conglomerate is taken as Lower Carboniferous, rocks of this age exist over quite a large area, making up most of the undulating country between Columbine Mountain and the Black Rock Range, and extending south to the Belubula River.

The conglomerate is quite a compact rock of a purple-brown colour, containing pebbles of quartzite. Most of the tuffs and mudstones are difficult to split along the bedding, show spheroidal weathering, and sometimes contain spheroidal concretions.

(5) *Tertiary.*

The most important rocks of Tertiary age are the basaltic and trachytic lavas which have issued forth from the volcanic centre of Mt. Canobolas. The trachytes occur within a distance of eight miles from Mt. Canobolas, but the basalts, having a much higher degree of fluidity, have flowed much further down old river valleys in a south-westerly direction towards Toogong and Long's Corner.

On Bowan Downs property, north-east of the Black Mountain, a trachytic basalt outcrops in the valley of a tributary of Paling Yards Creek. It appears to be overlain by a porphyritic trachyte, in which beds of trachyte breccia and diatomaceous earth occur. The phenocrysts are of glassy orthoclase, and the colour of these rocks varies from purple-brown to greenish grey. A dark, resinous, olivine trachybasalt overlies the porphyritic trachytes near " Bowan Downs ".

East of Canomodine Creek, too, porphyritic trachytes seem to overlie a basalt which is different to those making up the extensive flows of the Cudal and Toogong districts.

Fine-grained ægirine-trachytes are well developed east of the Black Mountain along the Cargo-Orange road. They have a dark blue-grey colour and resinous lustre when fresh, but readily alter to a grey or yellowish-brown, friable rock. Their stratigraphical position is uncertain, but they appear to be equivalent to the porphyritic trachytes.

The basalts of the Cudal and Toogong districts are probably the youngest of the Tertiary flows. They outcrop north of Cargo along Warree Creek and near Bowan Park ; and also along Gerybong, Oaky, Boree and Mandagery Creeks to the west.

The most common type is a dark, fine-grained rock with phenocrysts of glassy plagioclase which are often stained red by hæmatite. In places, the surface of the flow is vesicular and the vesicles are sometimes partly filled with chlorite, calcite or zeolites. At several localities there is evidence of two flows. One mile north of Cudal* the lower flow, a non-porphyritic basalt, rests on a grey decomposed rock, possibly a trachyte tuff. The upper flow is a basalt porphyritic in white plagioclase.

A generalized sequence of the Tertiary lavas, then, is probably as follows :

4. Basalts of the Cudal and Toogong districts.
3. Olivine trachybasalt (localized).
2. Porphyritic and fine-grained trachytes.
1. Fine-grained trachytic basalt.

Pre-basaltic sands and gravels, now quartzites and silicified conglomerates (" grey billy "), are found under and along the margins of the lavas. They also occur in isolated outcrops some distance away from the nearest basalt, indicating the original extent of the latter.

Near " Mandagery ", beside Mandagery Creek, silicified conglomerate and sandstone form a large, rounded outcrop more than 30 feet high. Smaller patches of " grey billy " and gravels occur at intervals along Boree and Mandagery Creeks as far as Long's Corner, and thence along the road to Burdett for about two miles.

Other sediments of doubtful age (but lying within the range of Tertiary to Recent) may be noted here.

At several localities (viz. in Barragan and Cargo Gullies, near " Eurella ", and in portion 18, Parish of Canomodine), finely-banded, orange-coloured clays occur, and in all except the last-named place they appear to underlie basalt. The clays are soft and sectile, however, and show no hardening or silicification.

White, friable sandstone occurs near the boundary of the Tertiary basalt west of Boree Creek and north of Barragan. Its relation to the basalt is uncertain, but it is probably of Tertiary age. Rocks of similar age and small extent include ferruginous sandstone and hæmatite north of Toogong and between Toogong and Barragan.

Although the sediments of the Gum Flat lead have been referred to a post-Tertiary age (Andrews and Morrison, 1915), it is possible that the lower sediments may be of late Tertiary age, as the time necessary for the accumulation of 370 feet of sediments, and later degradation of the alluvium to form a broad valley, must be considerable.

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* Information from bore cores.

No opportunity now exists to examine the sub-surface sediments but according to Andrews and Morrison they consist of "buried river wash and carbonaceous sediments with leaf imprints . . . Superimposed on these are great thicknesses of ferruginous sandy clays flanking an irregular but steeply pitching mass of coarse wash lying against the now-buried valley wall."

(6) *Quarternary.*

Deposits of this age are mainly gravels, ferruginous grit and more recent alluvium.

Characteristic of the limestone country are irregularly distributed areas of gravels, often firmly cemented by hæmatite and limonite. The gravels are best developed south of Cargo, where the limestone deposits are largest. The rounded pebbles are of quartz, quartzite and andesite, indicating that their source was some distance to the east.

The occurrence of these deposits overlying or near the margin of limestones, and their rare association with other rocks, suggests that channels were eroded in the limestone, and that iron-bearing solutions derived from the limestone cemented the gravels, lessening their ability to be transported, so that they remained in the position in which they were cemented.

Deposits of river gravels of post-basalt age occur between the Manildra-Toogong road and Mandagery Creek, and on the north side of Boree Creek, near Toogong. The latter deposit is up to 40 feet thick, and is related to the present course of Boree Creek. The original (pre-basalt) course of the creek is a short distance to the north of the present stream.

Most of the gravel deposits of Canomodine Creek are small, and occur up to 15 feet above the stream. A much higher deposit of gravels, on the north-eastern margin of the Cargo Creek limestone, has already been referred to in the Physiography section.

River and creek alluvium is well developed along the banks of the major streams and near the present source of Cargo Creek. Many of the smaller gullies show thicknesses of up to 30 feet of conglomerates, gravels, sands and clays.

(IV) STRUCTURAL GEOLOGY.

(*a*) *Folding.*

(i) *Ordovician.* The structure of the Ordovician rocks cannot be determined with certainty, because of the limited exposures. The strike, however, varies from meridional to east-north-east, so that there is probably an unconformity with the overlying Silurian rocks, similar to that recorded near Parkes (Andrews, 1910).

(ii) *Silurian.* The Silurian rocks are folded into a series of anticlines and synclines, with trend varying from north 12° east near Cudal to north 40° west south of Cargo. Both anticlines and synclines plunge either to the north or south, forming elongated domes and basins.

Between the Upper Devonian belts of the Nangar and Columbine Mountains, at least two major anticlines and two major synclines are present in the Silurian rocks; the distance between successive crests or troughs of folds being about five miles.

The folds are somewhat asymmetrical, with steeper dips on the eastern sides of anticlines. The angles of dip vary greatly, but are mostly between 25° and 60°. In general, the angles are greater in the Cargo district, for folding is closer there, and the area is heavily faulted.

The two major anticlines will be referred to as the Cudal-Barragan and Cargo anticlines; these are separated by the Avenel syncline, and another syncline occurs east of Cargo.

The Cudal-Barragan anticline corresponds north of Cudal with the fold figured by Joplin and Culey (page 269, 1937). The trend one mile west of Cudal (where the oldest beds exposed are limestone and clayshales) is north 12° east. The fold continues to the south for 3½ miles until it is intersected by the Oaky Creek fault, where the axis is displaced half-a-mile to the west, and the strike changes abruptly to north 28° west. With this strike the fold continues in a southerly direction towards Barragan, where the strike changes to nearer meridional again. South of Barragan, the anticline plunges to the south, and the andesites (occupying the core of the anticline) disappear beneath the surface, giving place to the overlying tuffs.

On the western side of this anticline, successive beds dip to the west at angles between 25° and 50°, as far as Mandagery Creek, where the slates are highly cleaved, and appear to have steep angles of dip. The strike is not constant in the beds west of the anticlinal axis, varying from north 20° west to north 36° east. Minor drag folds occur in the clayshales.

The Avenel syncline north of Avenel is parallel to the Cudal-Barragan anticline, but to the south, where the Canomodine limestone begins to thicken, the strike changes from north 15° west to north 40° west. A minor anticlinal fold appears in the centre of the limestone belt, forming a dome-like structure.

In the vicinity of Gerybong Creek the strata are much disturbed due to the intrusion of a sill, which has lifted the surrounding rocks a distance of about 100 feet.

Folding in the Cargo Andesitic Series. Near Cargo the folding is closer and more complex, and approximates to an anticlinorium. North of Cargo, only isolated data on the strike and dip can be obtained, but in the highly dissected country to the south-east outcrops are better, and reliable information regarding structure may be ascertained from beds of stratified cherts and tuffs in the Andesitic Series.

The variation in strike and dip is shown in Fig. 1. It will be seen that at least three anticlines and two synclines occur across the width of outcrop of the Andesitic Series. The folds plunge to the south-east, and near the headwaters of Spring Creek the variation in strike indicates a steep angle of pitch. The most south-easterly of these folds (a plunging anticline) accounts for the curvature in the outcrop of the Cargo Creek limestone on the south side of Canomodine Creek.

The strike of the fold axes near Cargo varies from north 35° west to nearly north-south further east. On the eastern margin of the Andesitic Series the equivalent of the Cargo Creek limestone occurs in two plunging synclines. North of Canomodine Creek the fold plunges north; south of the creek it plunges south, but only the western side is preserved, as the eastern side has been cut off by a fault.

Between the south-eastern extremity of the Cargo Creek limestone and the Upper Devonian quartzites the strike of the fold axes is nearly north-south; except near the fault junction between andesites and limestone, where the strata curve around in a westerly direction.

(iii) *Upper Devonian and Lower Carboniferous.* Silurian and Upper Devonian rocks are separated by fault junctions in every part of the district except at the south-east corner, where good evidence exists of their mutual structural relations.

There, on the Belubula River, Upper Devonian quartzites striking 350° and dipping west at 17° overlie Silurian tuffs and slates with strike 10°, dipping west at 40°. An unconformity therefore exists, although in many places the trends of Silurian and Upper Devonian rocks are approximately parallel.

The Mandagery Range quartzites dip west along their eastern boundary, but south of Meranburn the strike changes from north-south to north-west

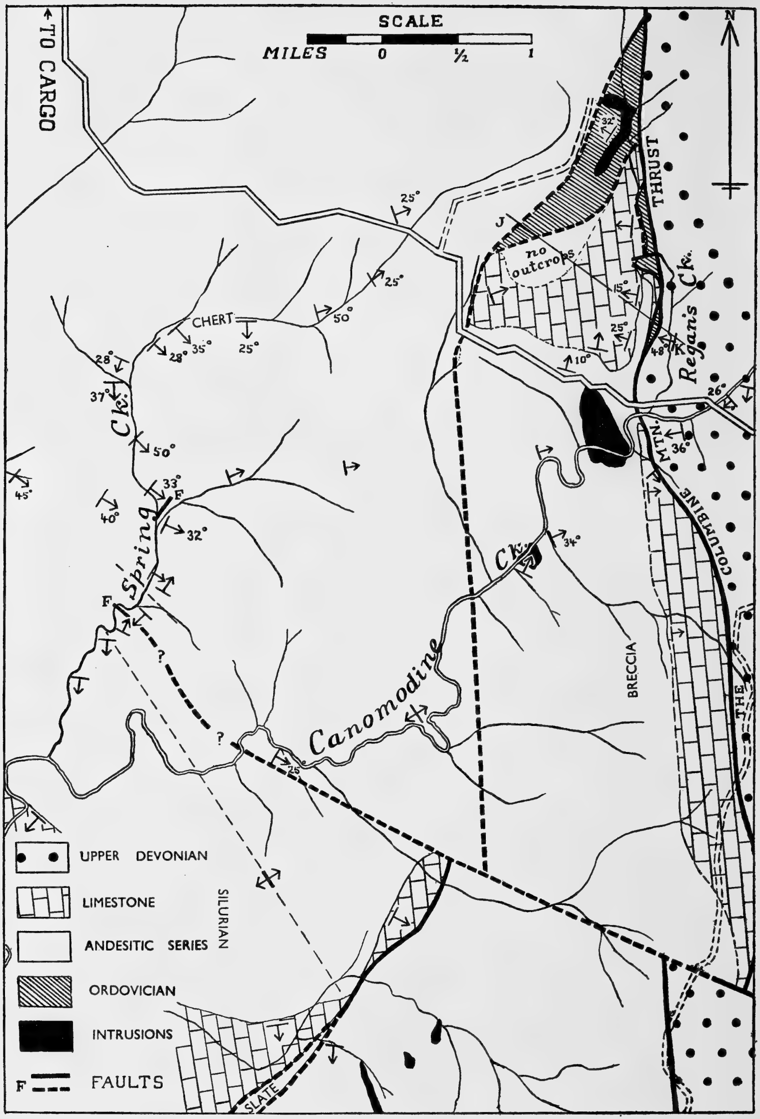


Fig. 1.—Map showing the structure south-east of Cargo.

south-east, indicating that the structure may be a large plunging syncline or basin.

On the eastern side of the district the structure in the Upper Devonian is again a syncline, with a dome developed on the western side of the fold.

Columbine Mountain is formed of quartzites occupying the central part of the dome, the axis of which has a north-south strike. Canomodine Creek exposes a section through the southern end of this dome, and the strike and dip varies gradually over a distance of half a mile.

The syncline is very asymmetrical, with a steeper western side. On the eastern side conglomerates form a gentle dip slope extending from the foothills of the Black Rock Range almost as far as Columbine Mountain. The structure becomes more complex to the south near Four Mile Creek, where a minor anticline and syncline appear, and outcrops are repeated by faulting.

Only the tuffs and mudstones are of definite Carboniferous age, and these appear to overlie the Upper Devonian rocks conformably.

At the Black Mountain, the structure in the Upper Devonian appears to be a plunging anticline or elongated dome. The western side has been cut off by a major fault, leaving a J-shaped outcrop of the Upper Series (mainly quartzites). Creeks cutting through the quartzites expose good sections. Angles of dip greater than 60° are frequent, and some overfolding has taken place. Shear zones in shaley sandstones have also been noted here.

(*b*) *Faulting.*

The Columbine Mountain Faults. An important fault zone along the western side of Columbine Mountain and the Black Mountain marks the junction between Silurian and Upper Devonian rocks, and in some places Ordovician strata appear in the faulted area.

The main line of faulting has a general north-south trend and has been traced north as far as Paling Yard Creek and south to the Belubula River. From reconnaissance work further south there is reason to believe that the fault continues towards Woodstock.

Evidence of the fault may be seen at several places, particularly at Regan's Creek (three miles south-east of Cargo) and on Paling Yards Creek.

On Regan's Creek, about 200 yards north of the Canangles Road, Upper Devonian quartzites, shales and mudstones outcrop along the creek bed, striking 12° and dipping westerly at 48°. On the west bank of the creek, 120 feet vertically above it, is the junction between Upper Devonian (or Lower Carboniferous ?) conglomerate and Silurian tuffs of the Andesitic Series, which underlie the equivalent of the Cargo Creek limestone. The limestone has a strike of 10° and dips west at 25–30°, so that it appears to overlie the Upper Devonian rocks.

A little further north, Ordovician slates appear at the boundary of the Upper Devonian strata. They are bounded to the west by a fault parallel to the main fault, and they adjoin a limestone which is at the top of the Andesitic Series, so that a considerable thickness of the Silurian is missing. Furthermore, a rapid thinning-out cannot be assumed, for the full sequence of the Andesitic Series occurs on the south side of the syncline.

Still further north the main limestone belt adjoins the Upper Devonian series, and because of an oblique thrust fault Ordovician cherts and slates appear once again on the west side of the major fault. Another oblique fault to the north brings the Andesitic Series against the Ordovician and Upper Devonian rocks (Fig. 2).

The evidence of the same major fault is equally strong on Paling Yard Creek, where shales of the Lower Series of the Upper Devonian appear to dip beneath the equivalent of the Cargo Creek limestone. The limestone occurs in a narrow plunging syncline, and overlies (on the west side of the fault) a great thickness of the Andesitic Series.

Canangle Creek exposes a section through the quartzites which shows a gradual overturning of the strata as the fault is approached. This, together with the exposure of the actual fault plane in Regan's Creek, indicates that the major fault is a high angle thrust; Silurian rocks have been thrust over Upper Devonian and the downthrow side is the eastern side.

It is difficult to classify the other faults in the Regan's Creek area, but it is likely that normal and thrust faults alternate to produce the alternate strips of Silurian and Ordovician rocks. The most north-westerly of these oblique faults cuts off the limestone in the plunging syncline, then turns south through the Andesitic Series, where it is difficult to trace. It may join with the fault which terminates the south-eastern extent of the Cargo Creek limestone, but with this fault the upthrow side is to the east, not the west (see Fig. 1). The last-named fault turns south-east, cutting off the southern extent of the Andesitic Series, and ultimately joining the Columbine Mountain thrust near the Belubula River.

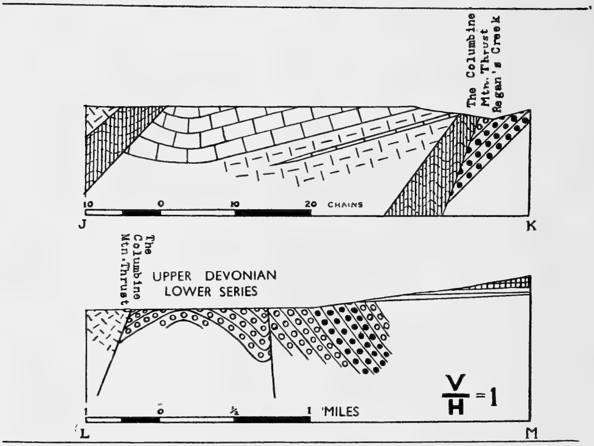


Fig. 2.—Sections across the Columbine Mountain Thrust.

An oblique fault five miles south-east of Cargo displaces both the faults just described. It strikes west 25° north, and offsets the Silurian-Upper Devonian boundary about 20 chains. The Cargo Creek limestone is also cut off by this fault.

On the eastern side of Columbine Mountain the angle of dip of the quartzites changes abruptly from a low angle to 65° (easterly) and successive strata are red shales, then conglomerates. It is likely that a bedding plane fault is present, dipping east.

The Canomodine Faults. Several faults occur near Canomodine Station, and some displace the boundary of the Canomodine limestone with the underlying beds.

The largest of these follows the course of Canomodine Creek for a short distance, and the actual fault junction may be seen on the west bank of Canomodine Creek downstream from the bridge, and on Back Creek near Canomodine Station. The strike is approximately west-south-west, and the south-east side is the downthrow side.

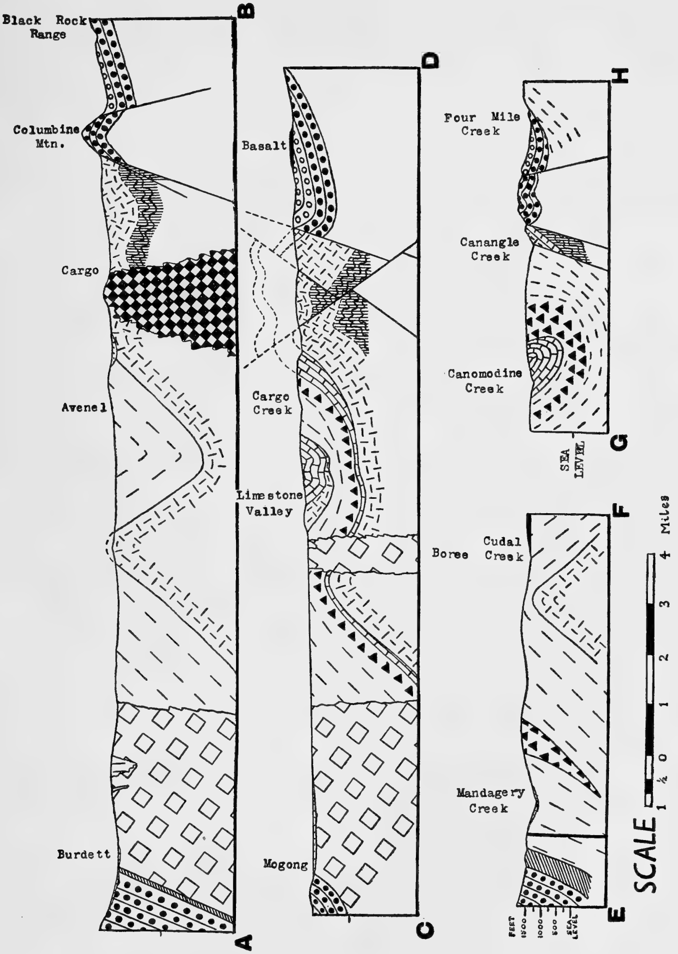


Fig. 3.

A smaller fault crosses the road one mile west of Canomodine. It has a strike of south 25° west, and displaces limestone and tuff beds about 400 yards.

Two other small faults affect the junction between the Canomodine limestone and the tuffs near the Cargo-Canowindra road.

The Oaky Creek Fault. In this case the fault plane is covered by alluvium and Tertiary basalt. The fault seems to trend east 30° north along Oaky Creek, thence in an east-west direction along Boree Creek.

The evidence for the presence of a fault along this line depends mainly on the sudden disappearance of the Andesitic Series and the displacement of the axis of the Cudal-Barragan anticline.

The axis, which, south of Oaky Creek, may reasonably be suspected to lie near the centre of the Andesitic Series, is displaced about three-quarters of a mile in a north-east direction north of Oaky Creek. Here, thin tuff beds occur in the core of the fold, these being at a higher horizon than the andesites. The downthrow side of the fault is to the north, as the southern side has been eroded to expose older beds. The abrupt change in strike is probably due to a horizontal movement of one block relative to the other, coupled with a slight rotary movement. A horizontal movement is postulated because no appreciable displacement of the anticlinal axis is to be expected, as the fault is approximately a dip fault. Alternatively, the horizontal displacement may be due to a westerly sloping axial plane.

The Shear Zone West of Mandagery Creek. A north-south zone of shearing exists in the uppermost Silurian sediments on the west side of Mandagery Creek. Slates have been converted to phyllitic rocks, and small intrusions of porphyry have suffered shearing. All the rocks in this zone show evidence of the introduction of solutions containing iron and silica ; the slates, and even the rhyolites, are jasperized in places, and quartz veins penetrate the Upper Devonian quartzites. The latter have steep dips, and sometimes show overfolding. The Lower Series of the Upper Devonian is missing along this line, probably due to faulting.

Numerous minor faults have been found throughout the district, but only two of these appear on the map (Plate XXI). These displace limestone beds south of the Cudal-Manildra road.

The Age of the Faults. Both the Columbine Mountain fault and the Mandagery shear zone are post-Upper Devonian, pre-Tertiary. As Lower Carboniferous strata are conformable with the Upper Devonian, the diastrophic epoch to which these faults belong must be placed between the close of Lower Carboniferous and the Tertiary period. The folding of the Upper Devonian rocks must also have taken place within this period.

The age of most of the other faults in the area is uncertain, and it is possible that some may have occurred between the end of the Silurian and the beginning of the Upper Devonian (e.g. the Oaky Creek fault).

Jointing. The directions of jointing vary greatly, as the trends of the folds vary, and local folding and faulting complicate the patterns. Near Cargo the dominant jointing is east-west and north-east south-west in the Andesitic Series, and igneous dykes to the north follow these directions.

V. INTRUSIVE ROCKS.

Nearly all the intrusive rocks of the district invade Silurian strata, and so far none has been found invading Upper Devonian rocks. The age of the intrusives seems to be within the period between the close of the Silurian and the beginning of the Upper Devonian ; probably late Middle Devonian.

(1) *Quartz Porphyries and Granite Porphyry.*

Near Dulladerry Creek two acid dykes invade the Upper Silurian slates. They are both composed of a pale grey felsitic rock, with small phenocrysts of quartz and felspar, and resemble the more leucocratic of the rhyolites. It is possible that they were feeders to these flows, and are of late Silurian age.

The intrusion at Cargo is in the form of a small boss of acid hypabyssal types. It has been suggested that the rocks may be a pre-Silurian inlier (Andrews and Morrison, 1915), but definite intrusive relations with the Andesitic Series have been found in several gullies near the Cargo-Canowindra road.

At least two main types of rock are present; one a quartz porphyry, with or without felspar phenocrysts, the other a felsite, with a few small phenocrysts of acid plagioclase. The quartz porphyries contain phenocrysts of idiomorphic quartz and felspar in a cream or grey aphanitic groundmass. Pyrites is usually present, and may replace the altered felspar. The felsites are of the same colour, but do not show quartz phenocrysts. The intrusion is tentatively assigned a late Silurian age, because of its affinities with the acid dykes of Dulladerry Creek.

On the Cudal-Manildra road 3½ miles north-west of Cudal, a small boss of quartz felspar porphyry invades the Silurian clayslates. Phenocrysts of white, albitized felspar, pink orthoclase and brown vitreous quartz are set in a dark grey stony groundmass. Some varieties resemble the Manildra granite porphyry, and it is considered that the intrusion is a phase of this rock type.

The typical granite porphyry of Manildra has been found at only one place in this district, viz. four miles north-east of Toogong. The rock contains large idiomorphic phenocrysts of quartz, pink felspars and chloritized biotite, in a pink, fine-grained to aphanitic groundmass.

An intrusive mass of quartz keratophyre invades the Silurian slates north of Sterling Public School. The intrusion is in the form of a sill, for both overlying and underlying clayslates have been converted to hornfelses. The base of the sill is at the level of Gerybong Creek, and the igneous rock forms a cliff about 100 feet high, capped by silicified sediments.

In most places the rock is very fine-grained, resembling the felsite of the Cargo intrusion. Thin sections show small phenocrysts of albite, quartz and orthoclase in a cryptocrystalline, partly glassy groundmass.

(2) *Granophyres and Porphyrites.*

Acid hypabyssal rocks ranging from microgranite to augite-rich granophyre occur in a discontinuous dyke extending from Mandagery Creek north of Toogong to a point 1½ miles north-east of Cargo.

The strike varies from north 40° west at "Derowie" to east-west near Cargo. Only isolated lenticular outcrops occur, and the maximum width of the intrusion is eight chains. North-east of Cargo the dyke is intersected by a dyke of monzonite porphyry striking north 48° east. The dykes have been injected along dominant joint planes in the country rock.

The typical granophyre is a pink rock with small phenocrysts of sericitized plagioclase in a fine-grained granophyric groundmass containing orthoclase, quartz, biotite, and sometimes augite. A related rock type, an augite porphyrite from west of Sterling Public School, probably belongs to the same dyke. It has been intersected by a later dyke of porphyritic dolerite. Granophyres have also been found near Bowan Park, and north-east of Canomodine.

The monzonite porphyry has large phenocrysts of pale green chloritized plagioclase and prismatic augite in a fine-grained pink groundmass of plagioclase, augite and orthoclase. A similar rock occurs at the margin of the granophyre in some parts of the east-west dyke, and is of a slightly earlier age. The porphyrite which invades Ordovician slates in Regan's Creek (east of Cargo) is related to these rocks.

All these hypabyssal types have been subjected to intense deuteric alteration, with the production of chlorite, sericite, kaolin, albite, epidote and prehnite.

(3) *The Garnetiferous Porphyry.*

A quartz felspar porphyry with sparsely distributed red garnet occupies large areas south of Toogong. It also occurs between Meranburn andToogong, and south of Cargo.

In hand specimen the rock is of a medium grey colour, with phenocrysts of white felspar, colourless quartz and chloritized biotite or hornblende.

Similar rocks from the Wellington district have been described as garnetiferous tuffs (Basnett and Colditz, 1945). However, the rocks show intrusive relations in the Cargo district, and there is some evidence for regarding them as intrusive porphyries. They are equivalent to the so-called " intrusive tuffs ", which are a feature of the Silurian igneous activity in other parts of New South Wales (Browne, 1929).

(4) *Dolerites.*

Doleritic intrusions occur throughout the district in dykes and small bosses. Except for the porphyritic dolerite previously noted, the dyke rocks are fresh, ophitic types, whereas the dolerites of the bosses have suffered much deuteric alteration.

The porphyritic dolerite occurs in a north-south trending intrusion west of Sterling Public School. The rock has phenocrysts of plagioclase and augite in a fine-grained, grey, doleritic groundmass.

Small bosses of dolerite occur north-west of Cudal and on Canomodine Creek, south-east of Cargo. They are medium-grained rocks consisting of pyroxene, plagioclase and a little apatite and sphene, with deuteric minerals chlorite, calcite and epidote. Magnetite or ilmenite is usually present, and some quartz is usually set free by deuteric activity.

The dolerites occurring in dykes are mostly very similar, fine to medium-grained types consisting mainly of plagioclase and augite in ophitic or sub-ophitic relationship. A rock from a dyke on Mandagery Creek (west of Cudal) has small amygdules of calcite and chlorite, while another to the south contains quartz and micropegmatite, with ilmenite, sphene and apatite.

A most unusual dyke rock from Canangle Creek shows large phenocrysts of hornblende, and occasionally plagioclase. It varies from a hornblende porphyrite to a hornblende lamprophyre, according to the percentage of plagioclase present as phenocrysts.

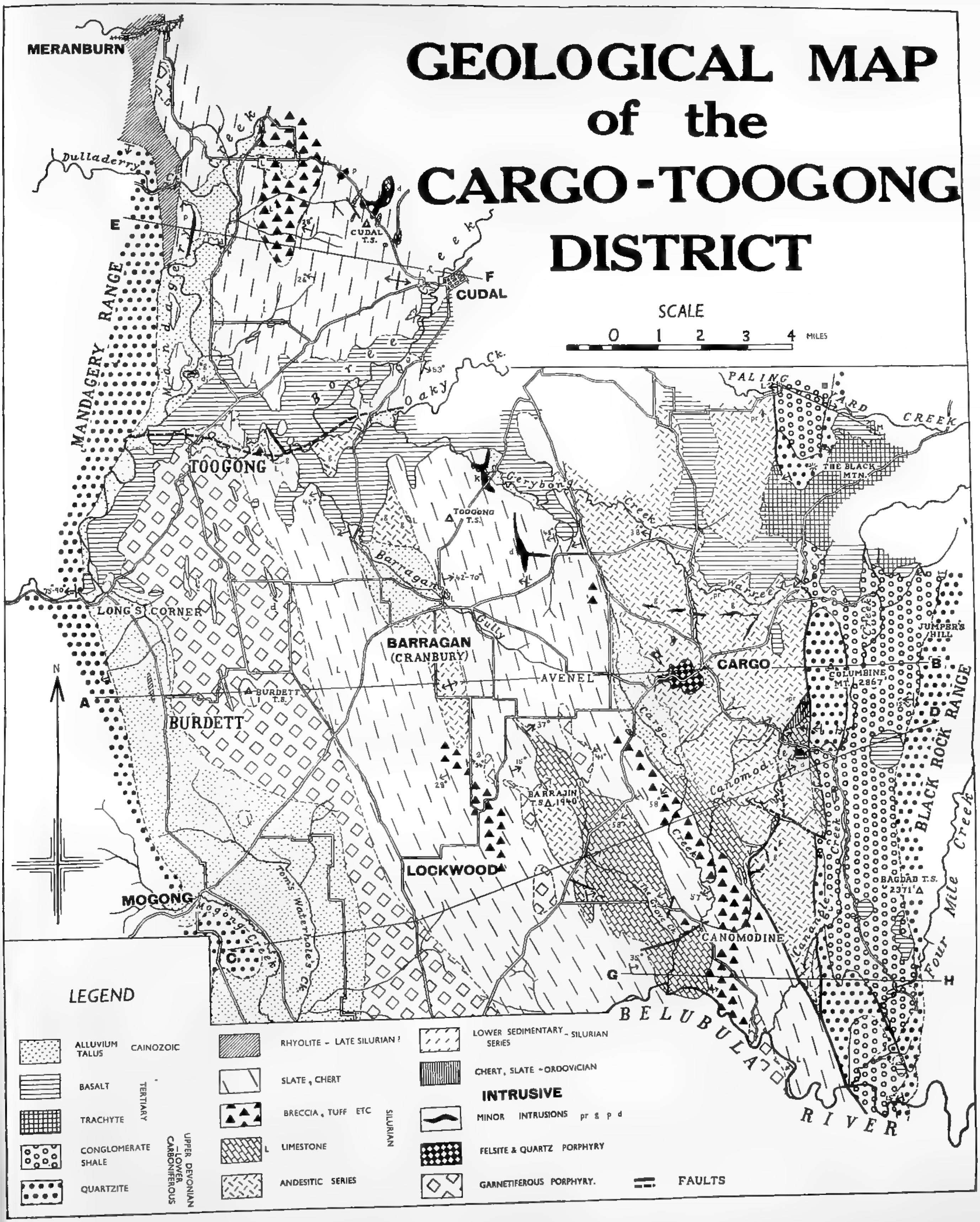
VI. SUMMARY.

Most of the stratified rocks of the Cargo-Toogong district are of Silurian and Upper Devonian age. They have been folded into plunging anticlines and synclines, which, when a large area is considered, show themselves to be greatly elongated domes and basins. A great deal of faulting has taken place, especially along the boundaries of Silurian and Upper Devonian rocks.

Points of some structural and stratigraphical significance are: (1) the unconformity between Silurian and Upper Devonian rocks; (2) the discovery of Lower Carboniferous strata and their apparent conformity with the Upper Devonian.

Numerous minor intrusions invade the Silurian rocks, and these have been briefly noted. A peculiar garnet-bearing rock, previously described as a tuff further north, seems to show intrusive relations.

Tertiary lavas partly cover the older rocks, and have flowed down old river valleys from the direction of Mt. Canobolas. The chief types are basalts, but trachytes become more abundant closer to the volcanic foci.


GEOLOGICAL MAP
of the
CARGO-TOOGONG
DISTRICT
SCALE
0 1 2 3 4 MILES
N
MERANBURN
Dulladerry Ck.
Mandagery Ck.
Boree Ck.
Oaky Ck.
CUDAL
CUDAL T.S.
MANDAGERY RANGE
TOOGONG
TOOGONG T.S.
Gerybong Creek
Barragan Gully
BARRAGAN (CRANBURY)
AVENEL
LONG'S CORNER
BURDETT
BURDETT T.S.
MOGONG
Mogong Creek
Toms Waterholes Ck.
LOCKWOOD
BARRAJIN T.S. 1940
CARGO
Cargo Creek
Canomodine Creek
The Grove Ck.
CANOMODINE
PALING YARD CREEK
THE BLACK MTN.
Warree Ck.
JUMPER'S HILL
COLUMBINE MT. 2867
BLACK ROCK RANGE
BAGDAD T.S. 2371
Four Mile Creek
Canoble Ck.
BELUBULA RIVER
A
B
C
D
E
F
G
H
LEGEND
ALLUVIUM TALUS CAINOZOIC
BASALT
TRACHYTE
TERTIARY
CONGLOMERATE SHALE
QUARTZITE
UPPER DEVONIAN – LOWER CARBONIFEROUS
RHYOLITE – LATE SILURIAN ?
SLATE, CHERT
BRECCIA, TUFF ETC
L LIMESTONE
ANDESITIC SERIES
SILURIAN
LOWER SEDIMENTARY SERIES – SILURIAN
CHERT, SLATE – ORDOVICIAN
INTRUSIVE
MINOR INTRUSIONS pr g p d
FELSITE & QUARTZ PORPHYRY
GARNETIFEROUS PORPHYRY.
FAULTS

VII. ACKNOWLEDGEMENTS.

I wish to acknowledge the help and advice given by Dr. G. A. Joplin, who introduced me to this interesting area, and I am also indebted to other members of the staff of the Geology Department of the University of Sydney and to Dr. A. B. Walkom and Mrs. K. Sherrard.

For hospitality during field work, my thanks are due to Mr. and Mrs. V. T. O'Connell and Mrs. C. Wythes and family, of Cargo ; and to Mr. and Mrs. H. J. Balcomb and family and Mr. and Mrs. N. H. Balcomb of Toogong.

During the field work, I was accompanied on one occasion by Mr. G. M. Dimmock, and on another occasion by Messrs. T. G. Vallance and K. R. Sharp.

The work was carried out during the tenure of Deas-Thomson Scholarships at the University of Sydney, and financial assistance was obtained from a Commonwealth Research Grant.

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EXPLANATION OF PLATE XXI.

Geological Map of the Cargo-Toogong District.

Note.—The minor intrusions are lettered g, p, pr and d, denoting rock types related to granophyre, porphyry, porphyrite and dolerite respectively.

ABSTRACT OF PROCEEDINGS

OF THE

Royal Society of New South Wales

April 7th, 1948.

The Annual Meeting, being the six hundred and forty-eighth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

The Acting-President, Dr. F. Lions, was in the chair. Eighty-five members and visitors, including the senior Trade Commissioner for Canada, Mr. C. W. Croft, were present. The minutes of the previous meeting were read and confirmed.

The following were elected officers and members of the Council for the coming year :

President :

R. L. ASTON, B.Sc., B.E. (*Syd.*), M.Sc., Ph.D. (*Camb.*), A.M.I.E. (*Aust.*).

Vice-Presidents :

J. A. DULHUNTY, D.Sc.
F. LIONS, B.Sc., Ph.D., A.R.I.C.
D. P. MELLOR, D.Sc., F.A.C.I.
F. R. MORRISON, A.A.C.I., F.C.S.

Hon. Secretaries :

O. U. VONWILLER, B.Sc., F.Inst.P.
H. W. WOOD, M.Sc., A.Inst.P., F.R.A.S.

Hon. Treasurer :

A. BOLLIGER, Ph.D., F.A.C.I.

Members of Council :

R. C. L. BOSWORTH, M.Sc., D.Sc. (*Adel.*), Ph.D. (*Camb.*), F.A.C.I.
IDA A. BROWN, D.Sc.
R. O. CHALMERS, A.S.T.C.
F. P. J. DWYER, D.Sc.
H. O. FLETCHER.
F. N. HANLON, B.Sc.
C. J. MAGEE, D.Sc.Agr. (*Syd.*), M.Sc. (*Wis.*).
C. St. J. MULHOLLAND, B.Sc.
D. J. K. O'CONNELL, S.J., M.Sc., F.R.A.S.
W. B. SMITH-WHITE, M.A. (*Cantab.*), B.Sc. (*Syd.*).

The Annual Balance Sheet and Revenue Account were submitted to members by the Honorary Treasurer, and, on the recommendation of Dr. G. D. Osborne, seconded by Mr. J. Wallis Powell, were adopted.

THE ROYAL SOCIETY OF NEW SOUTH WALES.

BALANCE SHEET AS AT 29th FEBRUARY, 1948.

LIABILITIES.

1947.					1947.		
£		£	s.	d.	£	s.	d
92	Accrued Expenses				188	7	8
15	Subscriptions Paid in Advance				25	4	0
60	Life Members' Subscriptions—Amount carried forward				102	0	0
—	James Cook and Edgeworth David Medals—Amount carried forward				200	0	0
	Trust and Research Funds (detailed below)—						
	Clarke Memorial	1,928	3	8			
	Walter Burfitt Prize	1,097	7	10			
	Liversidge Bequest	725	15	0			
	Monograph Capital Fund	3,421	13	4			
6,996					7,172	19	10
25,979	ACCUMULATED FUNDS				25,877	0	11
(902)	Contingent Liability—In connection with perpetual leases granted to Australian National Research Council and the Pharmaceutical Society of N.S.W.—Maximum Liability £901 16s. 8d.						
£33,142					£33,565	12	5

ASSETS.

1947.					1947.		
£		£	s.	d.	£	s.	d.
293	Cash at Bank and in Hand				595	17	10
	Investments—Commonwealth Bonds and Inscribed Stock, etc.—at Face Value—						
	Held for—						
	Clarke Memorial Fund	1,800	0	0			
	Walter Burfitt Prize Fund	1,000	0	0			
	Liversidge Bequest	700	0	0			
	Research Fund	3,000	0	0			
	General Purposes	4,360	0	0			
10,860					10,860	0	0
61	Prepayment				160	10	6
	Debtors for Subscriptions	117	12	0			
	Deduct Reserve for Bad Debts	117	12	0			
—					—		
14,715	Science House—One-third Capital Cost				14,715	0	0
6,800	Library—At Valuation				6,800	0	0
373	Furniture—At Cost—*less* Depreciation				396	10	1
30	Pictures—At Cost—*less* Depreciation				28	14	0
10	Lantern—At Cost—*less* Depreciation				9	0	0
£33,142					£33,565	12	5

TRUST AND MONOGRAPH CAPITAL FUNDS.

	Clarke Memorial. £	s.	d.	Walter Burfitt Prize. £	s.	d.	Liversidge Bequest. £	s.	d.	Monograph Capital Fund. £	s.	d.
Capital at 28th February, 1947 ..	1,800	0	0	1,000	0	0	700	0	0	3,000	0	0
Revenue—												
Balance at 28th February, 1947	108	13	8	65	7	10		—		322	8	4
Interest for twelve months ..	64	13	9	34	15	0	25	15	0	99	5	0
	173	7	5	100	2	10	25	15	0	421	13	4
Deduct Expenditure ..	45	3	9	2	15	0		—			—	
Balance at 29th February, 1948 ..	£128	3	8	£97	7	10	£25	15	0	£421	13	4

ACCUMULATED FUNDS.

	£	s.	d.	£	s.	d.
Balance at 28th February, 1947				25,978	10	3
Less—						
Deficit for twelve months (as shown by Income and Expenditure Account)	£81	11	4			
Increase in Reserve for Bad Debts	19	18	0			
				101	9	4
				£25,877	0	11

G. D. OSBORNE,
Hon. Treasurer.

The above Balance Sheet has been prepared from the books of account, accounts and vouchers of the Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 29th February, 1948, as disclosed thereby. We have satisfied ourselves that the Society's Commonwealth Bonds and Inscribed Stock are properly held and registered.

HORLEY & HORLEY,
Chartered Accountants (Aust.).

Prudential Building,
39 Martin Place,
Sydney, 24th March, 1948.

INCOME AND EXPENDITURE ACCOUNT.
1st March, 1947, to 29th February, 1948.

1946-7.			1947-8.					
£			£	s.	d.	£	s.	d.
355	To Printing and Binding Journal—Vol. 80		506	19	0			
363	,, Salaries		361	10	0			
125	,, Library—Purchases and Binding		150	4	4			
68	,, Printing—General		89	17	4			
103	,, Miscellaneous		127	8	2			
95	,, Postage and Telegrams		95	0	8			
43	,, Rent—Science House Management Committee		45	15	11			
40	,, Cleaning		37	0	0			
22	,, Depreciation		23	7	0			
19	,, Telephone		18	19	10			
15	,, Insurance		15	3	7			
13	,, Audit		18	18	0			
8	,, Electricity		11	19	11			
—	,, Repairs		17	18	0			
	,, Reprints—							
	Expenditure	£205 13 3						
	Less Received	89 12 11						
			116	0	4			
	,, Annual Dinner—							
	Expenditure	£69 8 7						
	Less Received	48 15 0						
			20	13	7			
	,, Conversazione—Atomic Education—							
	Expenditure	£39 4 0						
	Less Received	8 0 0						
—			31	4	0			
1,269						1,687	19	8
255	,, Surplus for Twelve Months					—		
£1,524						£1,687	19	8

1946-7.		1947-8.		
£		£	s.	d.
522	By Membership Subscriptions	556	10	0
400	,, Government Subsidy	400	0	0
436	,, Science House—Share of Surplus	482	10	0
145	,, Interest on General Investments	156	18	4
6	,, Receipts from Reprints	—		
1	,, Other Receipts	—		
8	,, Proportion of Life Members' Subscriptions	10	10	0
6	,, Annual Dinner	—		
		1,606	8	4
—	,, Deficit for Twelve Months	81	11	4
£1,524		£1,687	19	8

The Annual Report of the Council (1947–48) was read, and on the motion of Dr. F. P. J. Dwyer, seconded by Mr. A. S. Le Souef, adopted.

Report of the Council, 1947-48 (Rule XXVI).

By resignation the Society has lost six members: Joan Marian Beattie, Reginald Frank Cane, Norman Augustus Faull, Jack Campbell Norrie, Douglas Elwood White and Guy Carrington Yates.

The membership now stands at 332, 25 new members having been elected during the year namely Peter Beckmann, Gregory Stewart Buchanan, Gladys Olive Curry, Alan Marchant Downes, Naida Sugden Gill, Stuart Frederick Gill, Neil Ernest Goldsworthy, Lennard Robert Hall, Justin Ernst Humpoletz, Raymond James Wood Le Fevre, James Charles Lloyd, Patrick Reginald McMahon, Charles Joseph Magee, Leo Edmund Maley, George E. Mapstone, Peter Nordon, Adrian Noel Old, Nancy Evelyn Ray, Reginald John Ray, Fritz Henry Reuter, Arthur Sinclair Ritchie, Bruce Ritchie, William Broderick Smith-White, Gordon Keyes Webb and Ronald Louis Werner.

Eleven ordinary meetings of the Council and one special meeting were held during the year commencing 1st April, 1947, at which the average attendance was 14. During the same period nine general monthly meetings were held, the average attendance being 35.

The special meeting of the Council was held to discuss arrangements for the Conversazione held on the 8th October, 1947, in connection with the Society's campaign on Atomic Education.

Election of Honorary Members.—The following were elected to honorary membership of the Royal Society of New South Wales at the annual and general monthly meeting held on 2nd April, 1947 : Sir Harold Spencer Jones, M.A., D.Sc., F.R.S., and Professor F. Wood Jones, D.Sc., M.B., B.S., F.R.C.S., L.R.C.P. (London), F.R.S., F.Z.S.

Election of Councillors.—Dr. F. P. J. Dwyer and Mr. W. B. Smith-White were elected to Council at the meeting held on the 27th August, 1947, in place of Mr. R. S. Nyholm and Miss P. Rountree, who had resigned from Council owing to their impending departure overseas.

Addition to Rule V.—The following addition has been made to Rule V (first paragraph) : " A copy of the list shall be posted to each financial member of the Society not less than ten days before the closing date for nominations." The addition has been made to ensure that members receive the list of Council's recommendations for office-bearers in ample time to submit further nominations if desired.

Thirty-five papers were accepted for reading and publication during the year, and the following short addresses and lecturettes were given :

" Submarine Canyons with special reference to recent discoveries off the South Australian Coast ", by G. D. Osborne, D.Sc. (Syd.), Ph.D. (Camb.).
" Some New American Research Tools ", by F. Lions, B.Sc., Ph.D., A.R.I.C.
" Stellar Energy ", by Harley Wood, M.Sc., A.Inst.P., F.R.A.S.
" Separation of Isotopes by Gaseous Diffusion ", by R. C. L. Bosworth, M.Sc., D.Sc. (Adel.), Ph.D. (Camb.), F.A.C.I., F.Inst.P.
" Radioactive Tracers in Chemistry ", by F. Lions, B.Sc., Ph.D., A.R.I.C.
" Palæontological Work in the U.S.A.", by I. A. Brown, D.Sc.
" Impressions of Chemical Research Activity in Britain ", by T. Iredale, D.Sc., F.R.I.C.

Films.—The following sound films were screened at the general meeting held on the 2nd July, 1947 :

" The Body Defences against Diseases."
" The Action of the Kidneys."
" Fuels and Heat."
" Light Waves and their Uses."

Exhibit.—At the general meeting held on the 7th May, 1947, an exhibit of " Synthetic Minerals used in Optical and other Scientific Apparatus " was given by F. M. Quodling, B.Sc.

Demonstration.—At the same meeting a demonstration of " Some Photo-chemical Properties of Tungstic Acid " was given by A. Bolliger, Ph.D., F.A.C.I.

Commemoration of Great Scientists.—At the general meeting held on 5th November, 1947, the following addresses were given :

(1) " Torricelli."
" Helmholtz." Enunciation of the Principle of the Conservation of Energy, by Mr. J. B. Thornton.

(2) " Semmelweiss." Prevention of Puerperal Fever.
" Simpson." Introduction of Chloroform Anæsthesia, by Dr. K. Brown.

Popular Science Lectures.—Five Popular Science Lectures were delivered during the months of May, June, August, September and October, and were greatly appreciated by the members of the Society and the general public.

May 15th.—" The Hunter River Valley—a Future T.V.A. ? " by W. H. Maze, M.Sc.

June 19th.—" Snakes and Snake Venom ", by J. R. Kinghorn, C.M.Z.S.

August 21st.—" Measuring the Face of a Continent—the Use of Radar and Photography in Mapping ", by R. L. Aston, B.Sc., B.E. (Syd.), M.Sc., Ph.D. (Camb.), A.M.I.E. (Aust.).

September 18th.—" The Colouring Matter of Plants ", by R. M. Gascoigne, M.Sc.

October 16th.—" The Story of Goitre ", by Hugh R. G. Poate, M.B., Ch.M. (Syd.), F.R.C.S. (Eng.), L.R.C.P. (Lond.), F.R.A.C.S.

Clarke Memorial Lecture.—The Clarke Memorial Lecture for 1947 was delivered by Professor H. S. Summers, D.Sc., on 17th July, 1947, the title being " The Teachers of Geology in Australian Universities ".

Clarke Memorial Medal.—The Clarke Memorial Medal was awarded to Dr. Hubert Lyman Clark, of the Hancock Foundation, University of Southern California, U.S.A., in recognition of his distinguished contributions to natural science, particularly in regard to the elucidation of the Echinodermata of Australia.

Walter Burfitt Prize.—The Walter Burfitt Prize was awarded to Dr. John Conrad Jaeger, of the University of Tasmania, Hobart, for outstanding contributions in the field of Mathematics.

James Cook and Edgeworth David Medals.—Through the generosity of Mr. H. F. Halloran, one of the oldest Life Members of the Society, two medals would be awarded by the Society :

(1) The James Cook Medal for outstanding contributions to Science and Human Welfare in the Southern Hemisphere. The first recipient of the James Cook Medal was Field Marshal the Rt. Hon. J. C. Smuts, P.C., C.H., K.C., D.T.D., LL.D., F.R.S., Chancellor of the University of Capetown and Prime Minister of the Union of South Africa.

(2) The Edgeworth David Medal, which would be awarded for distinguished scientific researches among younger workers.

Government Grant.—A grant of £400 was received from the Government of New South Wales. The Society greatly appreciates the Government's continued interest in its activities.

Finance.—The audit of the Society's accounts discloses that the finances are in a satisfactory condition.

Printing of Society's Journal.—Owing to increased cost of labour and material, the cost of printing the Society's Journal and Proceedings, as well as reprints of papers, has increased considerably. Previously the cost of the printing of the Journal, inclusive of reprints, was £13 per sixteen pages. Today's cost is £16, exclusive of reprints, per sixteen pages. This shows an increase of 23%, plus the extra charge for reprints.

Annual Dinner.—The Annual Dinner was held on the 1st April, 1948, at the Union Refectory, the University of Sydney. His Excellency the Governor-General and Miss Betty McKell were present, and the Minister for Education, the Honourable R. J. Heffron, represented the Premier and the State Parliament.

A total of 110 members and friends was present.

Science House.—The Royal Society's share of the profits in Science House during the period March 1st, 1947, to February 29th, 1948, was £482 10s., which represents the highest on record.

Science House Management Committee.—The Royal Society has had as its representatives at the meetings of the Management Committee of Science House Mr. H. O. Fletcher and Mr. F. R. Morrison, and as substitute representatives Dr. R. L. Aston and Mr. H. H. Thorne.

A.N.Z.A.A.S. Conference, Perth, W.A., 20th-27th August, 1947.—Mr. R. M. Gascoigne, Mr. R. S. Nyholm and the Rev. D. J. K. O'Connell were appointed as delegates to represent the Society.

Dr. Edgar Booth.—Dr. Booth, Chairman of the International Wool Secretariat, London, was welcomed in the Society's Reception Room on 16th April, 1947, on the occasion of his visit to Sydney. Dr. Booth referred to work being carried out by the International Wool Secretariat and discussed scientific liaison activities in relation to research and the wool industry.

Professor Raymond Firth.—Professor Firth, the eminent anthropologist, was welcomed in the Society's Reception Room on 22nd March, 1948.

Visit Overseas of the President, Dr. J. A. Dulhunty.—At a special meeting of the Executive Committee held in May, the President was granted leave of absence for the period of his visit abroad to confer with authorities on coal research and the coal industry. The visit was sponsored by the C.S.I.R., the University of Sydney and the B.H.P. Co. Ltd., and arrangements had been made for visits to England, the Continent and the U.S.A. During the President's absence from Sydney, Dr. F. Lions was appointed Acting President of the Society.

Monographs.—At the Council meeting held on the 30th June, 1947, it was decided to publish one or two Monographs per annum, on physical and biological sciences, the funds to be derived from the interest on the present Research Fund. The name of the latter had now been changed to the Monograph Capital Fund.

Payment to Authors.—As the period for payment of five shillings per page to authors had expired as from the 24th July, 1947, it was agreed that the costs of a draughtsman's services would be made available, if required, to authors of papers.

Conversazione.—A very successful conversazione was held on the 8th October, 1947. Following communications from the Association of Scientists for Atomic Education Inc. and the Emergency Committee of Atomic Scientists, headed by Professor Albert Einstein, the Society had decided to open its campaign on atomic education with the conversazione, at which short addresses were given by the Governor of New South Wales, the Chancellor of the University of Sydney, the Minister for Education and the Acting President. Many interesting exhibits were arranged, including a number by courtesy of the heads of departments at the University of Sydney and the C.S.I.R., the Colonial Sugar Refining Co. Ltd., the Sydney Technical College and the Museum of Technology and Applied Science. The Senate of the University of Sydney co-operated by making available the Great Hall for the function, and the Director of the Botanic Gardens assisted with the loan of palms.

The donation of the electrical wiring service to the exhibits by Mr. Churchill, and the services rendered by Mr. Baxter, Yeoman Bedell, and Staff were greatly appreciated.

Sidey Summer-time Medal.—At the request of the President of the Royal Society of New Zealand, the Sidey Summer-time Medal was presented to Dr. D. F. Martyn, of the Mt. Stromlo Observatory, Canberra, at the monthly meeting held on 5th November, 1947. The Medal had been awarded to Dr. Martyn for his work on radar and the receipt of radio waves from the sun.

Meetings of U.N.E.S.C.O., National Co-operating Committee.—Dr. R. L. Aston was chosen to represent the Royal Societies of Australia on the Scientific Co-operating Committee of U.N.E.S.C.O. The meetings, arranged by the Commonwealth Office of Education, were held on the 1st and 2nd March, 1948.

Dr. Aston stressed the need for representation of biological, as well as physical, sciences on the committee.

Collection of Pure Chemical Substances.—At the request of U.N.E.S.C.O., communicated through Professor J. Timmermans, of the University of Brussels, the Society is co-operating with the Australian National Research Council in implementing the proposal to build up a central collection of pure chemicals for the benefit of scientists all over the world.

Government Assistance for Fundamental Research in Australian Universities.—The Society informed the Federal Government that it gave full support to the request of the Australian National Research Council for increased government funds for fundamental research in Australian Universities.

The Library.—The amount of £57 0s. 5d. has been expended on the purchase of periodicals and the amount of £16 10s. spent on repairs to the lighting system ; the total sum spent on the Library over the past twelve months is therefore £73 10s. 5d. The binding for 1947-48 is not yet completed owing to lack of suitable cloth, which is imported, and consequently no account has been received from the bookbinders.

Exchanges.—The number of volumes now being sent to other societies is 387.

Accessions.—For the twelve months ending February, 1948, the number of accessions entered in the catalogue was 3,226 parts of periodicals.

Volumes on Loan to the Sydney Technical College Library.—A number of volumes representing incomplete sets were placed on loan to the Sydney Technical College Library for the benefit of Science students.

The loans have been made subject to conditions which will ensure every care being taken of the volumes.

Rationalization of the Libraries of the Linnean Society of New South Wales and the Royal Society of New South Wales.—During the past twelve months the Linnean Society of New South Wales has handed over to the Society's library all volumes requested under the rationalization scheme. On its side, the Royal Society of New South Wales has also given to the Linnean Society of New South Wales those volumes required to complete the Linnean Society's sets under the library rationalization scheme.

Reorganization of Library and Store.—The library and store have been reorganized, and new shelving has been erected for storage of journals for exchange and other publications.

Borrowers and Readers.—Members and visitors reading in the library numbered 17.

The number of books and periodicals borrowed by members, institutions and accredited readers was 285.

Among the institutions which made use of the arrangements for inter-library borrowing were : Food Preservation Laboratories, C.S.I.R., Drug Houses of Australia, Sydney University Medical Library, National Standards Laboratory, C.S.I.R., Fisher Library, C.S.I.R., Canberra, Colonial Sugar Technical Library, Sydney County Council Technical Library, Australian Paper Mills, Department of Public Health, Elliotts and Australian Drugs, Sydney Technical College, Royal Society of Tasmania, New England University College, Pastures Protection Board, McMaster Laboratories, M.W.S. and D. Board, Geology Department, University of Sydney Kraft Cheese, Forestry Department, Serum Laboratories, Melbourne, Melbourne University Library, Australian Glass Manufacturers, By-Products and Chemicals Ltd., Ministry of Post-War Reconstruction and Veterinary Research Station, Glenfield.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected members of the Society : Dorothy Carroll and Ilse Rosenthal-Schneider.

Election of Honorary Members.—The following were elected to honorary membership of the Society : Sir Robert Robinson and Professor Marcus Oliphant.

Clarke Memorial Medal.—The announcement was made of the award of the Clarke Memorial Medal for 1948 to Dr. A. B. Walkom.

Walter Burfitt Prize.—The announcement was made of the award of the Walter Burfitt Prize for 1948 to Dr. J. C. Jaeger.

James Cook Medal.—The announcement was made of the first award of the James Cook Medal to Field Marshal the Rt. Hon. J. C. Smuts.

Election of Auditors.—On the motion of Dr. Bosworth, seconded by Mr. Challinor, Messrs. Horley & Horley were re-elected as Auditors to the Society for 1948–1949.

Presidential Address.—As the President was abroad, the Acting President announced that Council had decided to ask the retiring President, Dr. J. A. Dulhunty, to deliver his address when he returned from overseas.

The following papers were read by title only : " A Gens of Dalmanitid Trilobites ", by E. D. Gill, B.A., B.D. ; " Occultations observed at Sydney Observatory during 1947 ", by W. H. Robertson, B.Sc. ; " A Cell for an 11½-inch Lens ", by H. W. Wood, M.Sc. ; " Micrometrical Measures of Double Stars ", by H. W. Wood, M.Sc. ; " The Paracloacal (Anal) Glands of *Trichosurus vulpecula* ", by A. Bolliger, Ph.D., and W. K. Whitten.

Address.—The Acting President welcomed Professor Griffith Taylor, Professor of Geography at the University of Toronto, formerly of Sydney University, who delivered an interesting address on the essential points of nation planning from a geographical, geological and physiographical viewpoint.

Dr. Lions, the Acting President, welcomed the newly elected President, Dr. R. L. Aston to the Presidential chair. Dr. Aston briefly acknowledged the honour.

A vote of thanks to Dr. Lions for his services to the Society as Acting President, in the absence of the President, was proposed by Professor Vonwiller, and was carried by acclamation

F. LIONS,
Acting President.

May 5th, 1948.

The six hundred and forty-ninth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. R. L. Aston, was in the chair. Forty-one members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of seven candidates for admission as ordinary members of the Society were read for the first time.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Leslie Arthur Cole, Kenneth George Mosher.

Popular Science Lecture.—It was announced that the first in the series of Popular Science Lectures would be given by Professor N. A. Burges on 20th May, 1948, and would be entitled " The Struggle between Fungi and Roots ".

Library.—The following accessions were received : 185 parts of periodicals, one purchase, two books, 27 back numbers.

The following paper was read :

" The Essential Oil of a Physiological Form of *Boronia ledifolia* (Gay) ", by A. R. Penfold, F.A.C.I., F.C.S., and F. R. Morrison, A.A.C.I., F.C.S.

Discussion.—The following papers were presented for discussion :

" A Cell for an 11½-inch Lens ", by H. W. Wood, M.Sc.

" A Survey of Anthocyanins in the Australian Flora ", by R. M. Gascoigne, E. Ritchie and D. E. White.

Exhibit.—" Bouncing Putty ", by Dr. D. P. Mellor.

June 2nd, 1948.

The six hundred and fiftieth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Vice-President, Mr. F. R. Morrison, was in the chair. Thirty-seven members and visitors were present. The minutes of the previous meeting were read and confirmed.

The deaths were announced of the following : George Frederick Birks, a member since 1923 ; Rev. Ernest Norman McKie, a member since 1932.

The certificates of nine candidates for admission as ordinary members of the Society were read for the first time.

The certificates of seven candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Paul Burke Andrews, Alan Victor Jopling, Frank Oswald Kimble, Harry Neil Scott Schafer, Kenneth Raeburn Sharp, Neville Cecil Stevens, Judith Zingel.

Extension Board Lectures.—An announcement was made in connection with the series of Extension Board lectures, the titles and dates as under :

" The Atom and Radioactivity ", by Dr. D. P. Mellor, 5th July, 1948.

" Artificial Transformations and Nuclear Fission ", by Dr. R. E. B. Makinson, 12th July, 1948.

" Atomic Physics and Human Welfare (Generation of Power : Radioactive Tracers) ", by Dr. F. Lions, 19th July, 1948.

" International Control of Atomic Energy ", by Dr. G. H. Briggs, 26th July, 1948.

Popular Science Lecture.—It was announced that the second in the series of Popular Science Lectures would be given by Dr. C. J. Magee, on Thursday, 17th June, 1948, and would be entitled " Plant Growth Regulators or Hormones ".

It was announced that a preliminary announcement of the Seventh Pacific Science Congress of the Pacific Science Association had been received. The Congress to be held at Auckland and Christchurch, New Zealand, February 2nd to 23rd, 1949.

It was announced that reprints published in the Society's Journal from 1904 to 1930 would be available to members, *gratis*, until the 30th June, 1948.

Library.—The following accessions were received : 273 parts of periodicals, 18 purchases, 62 back numbers.

The following papers were read :

" Spectroscopic Analysis of Alloy Steels ", by C. James. (Read by title only.)

" Nitrogen in Oil Shale and Shale Oil. Part I. The Nitrogen Compounds Present in Kerogen ", by Geo. E. Mapstone.

" Nitrogen in Oil Shale and Shale Oil. Part II. Organic Nitrogen Compounds in Shale Oil ", by Geo. E. Mapstone.

" Nitrogen in Oil Shale and Shale Oil. Part III. Nitrogenous Products from the Pyrolysis of Porphyrins and Proteins ", by Geo. E. Mapstone.

" Nitrogen in Oil Shale and Shale Oil. Part IV. Pyrolytic Reactions Involving the Formation and Decomposition of Tar Bases ", by Geo. E. Mapstone.

" Electro-Magneto-Ionic Optics ", by V. A. Bailey, M.A., D.Phil., F.Inst.P.

Discussion.—The following paper, previously read by title only, was presented for discussion :

" The Paracloacal (Anal) Glands of *Trichosurus vulpecula* ", by A. Bolliger, Ph.D., F.A.C.I., and W. K. Whitten.

Exhibit.—Enlarged photographs of the Second Positive Spectrum of Nitrogen showing some features of interest, by Professor O. U. Vonwiller and Miss D. P. Tarrant.

July 7th, 1948.

The six hundred and fifty-first General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. R. L. Aston, was in the chair. Fifty-two members and visitors were present. The minutes of the previous meeting were read and confirmed.

The death was announced of Ernest C. Andrews, a member since 1909 and President in 1921.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of nine candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Eric Harold Boyd, Joan Boyd, Cyril Lloyd Cook, John Cymerman, Oscar Le Maistre Knight, Lawrence Ernest Lyons, Ian Russell Sherwood, Ellice Simmons Swinbourne, Donald Francis Walker.

Clarke Memorial Lecture.—It was announced that the Clarke Memorial Lecture for 1948 would be delivered on Thursday, 15th July, 1948, at 8 p.m., by Sir Douglas Mawson, and would be entitled " The Sedimentary Succession of the Bibliando Dome : Record of a Prolonged Proterozoic Ice Age ".

It was announced that arrangements had been made to visit the National Standards Laboratory and the Radiophysics Laboratory on the 30th July, at 7.30 p.m., to see some of the things of interest in the laboratories.

It was also announced that in order to give all members opportunity of taking part in the business of Ordinary Monthly Meetings, the Council had decided to introduce some new features, such as Notes and Exhibits, at the meetings.

The Library.—The following accessions were received : 283 parts of periodicals, 20 purchases, 38 back numbers.

The following papers were read :

Presidential Address : " Some New Horizons in Coal Utilisation and Research ", by J. A. Dulhunty, D.Sc.

"Aspects of the Diels-Alder Reaction. Part III. A Note on the Reported Action with Anthraquinone", by R. M. Gascoigne and K. G. O'Brien. (Read by title only.)
"Contributions to the Study of the Marulan Batholith. Part I. The Contaminated Granodiorites of South Marulan and Marulan Creek", by G. D. Osborne, D.Sc., Ph.D. (Read by title only.)
"Nitrogen in Oil Shale and Shale Oil. Part V. The Determination of Nitrogen in Shale Oil and Oil Shale", by Geo. E. Mapstone. (Read by title only.)
"Nitrogen in Oil Shale and Shale Oil. Part VI. Acid Washing of Crude Shale Oil", by Geo. E. Mapstone. (Read by title only.)
"Nitrogen in Oil Shale and Shale Oil. Part VII. Distribution of Kerogen Nitrogen on Carbonization", by Geo. E. Mapstone. (Read by title only.)

August 4th, 1948.

The six hundred and fifty-second General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. R. L. Aston, was in the chair. Fifty-five members and visitors were present. The minutes of the previous meeting were read and confirmed.

The death was announced of Edward M. Wellish, a member since 1920.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Clive Melville Harris, Leo E. Koch, Joan W. Mulley, Betty Yvonne Taylor.

It was announced that the Liversidge Research Lecture would be delivered on Thursday, 19th August, 1948, by Professor Ian Lauder, and would be entitled "Some Recent Work on the Separation and Use of Stable Isotopes".

Request to Authors to Submit Abstracts with Papers.—The Council of the Society suggests to authors that when submitting papers they should give an abstract or summary suitable for publication in the Journal or for transmission to abstracting journals.

The visit to National Standards Laboratory and the Radiophysics Laboratory was reported upon.

The Library.—The following accessions were received: 247 parts of periodicals, 13 purchased parts, 30 back numbers.

The following paper was read:
"The Incomplete Nature of the Symmetry Relations between Thermodynamical Quantities", by R. C. L. Bosworth, D.Sc.

Discussion.—The following paper, previously read by title only, was presented for discussion:

"Contributions to the Study of the Marulan Batholith. Part I. The Contaminated Granodiorites of South Marulan and Marulan Creek", by G. D. Osborne, D.Sc., Ph.D.

Questions.—The following questions were answered:
"There is evidence that ice ages have occurred simultaneously in both hemispheres of the world—what is the evidence of this?" G. D. Osborne, D.Sc., Ph.D.
"What is a Transcendental Number?" Mr. W. B. Smith-White.
"What are Cosmic Rays?" Dr. R. E. B. Makinson.

September 1st, 1948.

The six hundred and fifty-third General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. R. L. Aston, was in the chair. Thirty-nine members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Eleonara Clara Gyarfas, Julius William Hogarth, Gordon Elliott McInnes, David Stanley Simonett.

Popular Science Lecture.—It was announced that the third in the series of Popular Science Lectures would be given by Mrs. C. Kelly, on Thursday, 16th September, 1948, and would be entitled "The Making of an Australian—A Study in Migration".

The Library.—The following accessions were received: 102 parts of periodicals, 27 purchased parts.

The following papers were read by title only:
"Occurrence of the Brachiopod Genus *Plectodonta* Kozlowski at Bowning, New South Wales", by I. A. Brown, D.Sc.

"Structural Data for the Northern End of the Stroud-Gloucester Trough", by G. D. Osborne, D.Sc., Ph.D., and P. B. Andrews.

"The Concepts of Resistance, Capacitance and Inductance in Thermal Circuits", by R. C. L. Bosworth, D.Sc., Ph.D.

Symposium.—The evening was devoted to a Symposium on "The Education of a Scientist". The following addresses were given:

"Science in Secondary Education", by Mr. J. B. Thornton.
"The Teaching of Science in the Universities", by Professor N. A. Burges.
"The Scientist and Scientific Method", by Professor K. E. Bullen.

October 6th, 1948.

The six hundred and fifty-fourth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. R. L. Aston, was in the chair. Forty-eight members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of seven candidates for admission as ordinary members of the Society were read for the first time.

The certificate of one candidate for admission as an ordinary member of the Society was read for the second time. The following person was duly elected an ordinary member of the Society: Charles A. M. Gray.

Popular Science Lecture.—It was announced that the fourth in the series of Popular Science Lectures would be given by Mr. N. A. Esserman on Thursday, 21st October, 1948, and would be entitled "Weights and Measures".

The Library.—The following accessions were received: 186 parts of periodicals, 18 purchases' 33 back numbers.

The following paper was read:

"Magnetic Properties of Some Tungsten Bronzes", by P. M. Stubbin and D. P. Mellor, D.Sc.

The following papers were read by title only:

"Coordination Compounds of Copper. Part I. Complex Copper (II) Cuprates (I)", by Clive M. Harris.
"Disproportionation Equilibria in Alkaline Earth Ions", by Noel Hush.
"Geology of the North-Western Coalfield, N.S.W. Part IV. Geology of the Gunnedah-Curlewis District", by F. N. Hanlon, B.Sc., Dip.Ed.
"Geology of the North-Western Coalfield, N.S.W. Part V. Geology of the Breeza District", by F. N. Hanlon, B.Sc., Dip.Ed.
"Geology of the North-Western Coalfield, N.S.W. Part VI. Geology of the South-Western Part of County Nandewar", by F. N. Hanlon, B.Sc., Dip.Ed.

Discussion.—The following addresses, delivered at the previous meeting by Mr. J. B. Thornton, Professor N. A. Burges and Professor K. E. Bullen, on "The Education of a Scientist", were presented for discussion:

"Science in Secondary Education",
"The Teaching of Science in the Universities",
"The Scientist and Scientific Method".

After a widely ranging discussion with many participating, Mr. Thornton and Professor Bullen made brief replies.

Questions.—The following questions were answered:

"Why are there black and white races?" Professor A. P. Elkin.
"Why does the moon always turn the same face towards the earth?" Mr. Harley Wood.

November 3rd, 1948.

The six hundred and fifty-fifth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. R. L. Aston, was in the chair. Forty-one members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificates of seven candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Fred Roy Blanks, Shirley Kathleen Doyle, Bruce Thomas Dunlop, Edward Carson Gardiner, Kenneth Roderick Glasson, Jean Northcott, Hubert Roy Perry.

Nuffield Foundation Dominion Travelling Fellowships.—It was announced advice had been received regarding the Nuffield Foundation Dominion Travelling Fellowships. The awards available would be as follows:

Three Fellowships in Medicine.
Two Fellowships in the Natural Sciences.
One Fellowship in the Humanities.
One Fellowship in the Social Sciences.

The Library.—The following accessions were received: 104 parts of periodicals, nine purchases.

The following papers were read by title only:

"Synthesis of Dithiohexestrol Dimethyl Ether", by G. K. Hughes and E. O. P. Thompson.
"Some Effects of Compression on the Physical Properties of Low-Rank Coal", by J. A. Dulhunty, D.Sc.

Commemoration of Great Scientists.—The following addresses were given:

Simon Stevin (Stevinus), born 1548, by Mr. H. H. Thorne.
Berzelius, died 1848, by Mr. J. B. Thornton.
Important Events in the History of Public Health—Quarantine and the Board of Health established in Venice, 1348, and the First Public Health Act of England, 1848, by Professor Harvey Sutton.

December 1st, 1948.

The six hundred and fifty-sixth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Vice-President, Mr. F. R. Morrison, was in the chair. Forty-seven members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Geoffrey William Anderson, Leonard Paul Ross.

International Congress of Biochemistry.—It was announced that a circular had been received advising that the International Congress of Biochemistry would be held at Cambridge, England, on August 19th to 25th, 1949.

International Congress of Mathematicians.—It was announced that a circular had been received advising that the International Congress of Mathematicians would be held at Cambridge, Massachusetts, U.S.A., on August 30th to September 6th, 1950.

Library.—The following accessions were received: 176 parts of periodicals and nine purchases.

The following papers were read:

"Coordination Compounds of Copper. Part I. Complex Copper (II), Cuprates (I)", by C. M. Harris.
"Mineralogical Examination of Soils Developed on the Prospect Hill Intrusion, New South Wales", by R. Brewer, B.Sc. (Read by title only.)
"Relations of Rank to Inherent Moisture of Vitrain and Permanent Moisture Reduction on Drying", by J. A. Dulhunty, D.Sc. (Read by title only.)
"The Chemistry of Bivalent and Trivalent Rhodium. Part XI. The Potential of the Trivalent Quadrivalent Rhodium Couple in Sulphuric Acid", by F. P. Dwyer, D.Sc., and H. N. Schafer, B.Sc.
"Geology of the North-Western Coalfield, N.S.W. Part VII. The Geology of the Boggabri District", by F. N. Hanlon, D.Sc., Dip.Ed. (Read by title only).
"Geology of the North-Western Coalfield, N.S.W. Part VIII. The Geology of the Narrabri District", by F. N. Hanlon, B.Sc., Dip.Ed. (Read by title only.)
"Note on the Occurrence of Tridymite in Metamorphosed Hawkesbury Sandstone at Bundeena and West Pymble, Sydney District, New South Wales", by G. D. Osborne, D.Sc., Ph.D.
"The Stratigraphy and General Form of the Timor Anticline, N.S.W.", by G. D. Osborne, D.Sc., Ph.D., A. V. Jopling, B.E., B.Sc., and F. W. Lancaster, B.E., B.Sc.
"Geology of the Canowindra District, N.S.W. Part I. Stratigraphy and Structure of the Cargo-Toogong District", by N. C. Stevens. (Read by title only.)

Questions.—The following questions were answered:
"What is the principle of the electron Microscope?" by Mr. R. L. Werner.
"What was the cause of the change of longitude of Sydney Observatory amounting to some 166 yards in about the year 1932, as indicated by certain one-inch military maps?" by Mr. Harley Wood.

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

GEOLOGY

Chairman : Mr. C. St. J. Mulholland.
Honorary Secretary : Mr. R. O. Chalmers.

Meetings.—Six meetings were held during the year, the average attendance being fourteen members and six visitors.

April 16th.—Address by Mr. F. N. Hanlon on " The Geology of the Willow Tree-Murrurundi District, with special reference to the age of the Werrie Basalts ".

May 21st.—Notes and Exhibits : By Miss Quodling : (*a*) Contact magnetite rich phase with chert, from Prospect ; (*b*) Crystal models made by pouring molten sulphur into Teclex (a colloidal, flexible moulding material used in dental work). By Mr. Stevens : Three new central western localities for graptolites : (*a*) two localities near Woodstock ; (*b*) Cargo. By Mr. C. St. J. Mulholland : " A Review of Recent Work of the Geological Survey." By Mr. H. O. Fletcher : " Recent Fossil Discoveries in Triassic Rocks of the Sydney District." By Mr. R. O. Chalmers : " New Meteorites from New South Wales."

July 23rd.—Exhibit : By Mrs. Sherrard : Specimens of *Monograptus bohemicus* (Barrande) from shale beneath the Dalmanites (Middle Trilobite) bed of the Hume series of the Upper Silurian at Hatton's Corner, Yass, N.S.W.

Address by Dr. Leo Koch : " A New Type of Schedules for Geological and Mineralogical Field Investigations (based on the System of the Categories of Natural Science)." A system of categories has been developed, similar to that of Aristotle's Table of Categories, but worked out as the " System of the Ultimate Modes of Being of Natural Units as Perceived through the Senses ". The highest principles of division and grouping of the new system are the forms of apprehension, space and time. The system is called " Tetraktys ", because of the fourfold, partly tetrahedral, configuration of its parts and elements.

When the whole content of the " Schedule for the Field Description of Sedimentary Rocks " (*Bull. Am. Assoc. Petroleum Geologists*, Vol. 6, pp. 254-259, 1922) is projected on to forms showing the pattern of the Tetraktys (facts belonging to petrography, mineralogy, palæontology, etc., being projected separately) then approximately half of the categories or categorical concepts of the Tetraktys are covered by corresponding elements of the " Schedule " mentioned above. The " System of the Categories of Natural Science ", therefore, when applied to objects of the geological science, shows the totality of the categories of geological field observations possible by means of the unaided senses.

The system can likewise be used for checking the completeness of any other geological and mineralogical features.

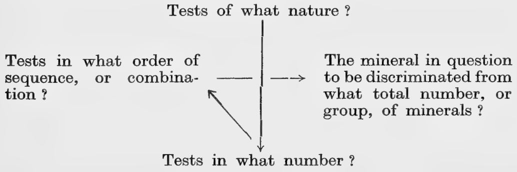
August 27th.—Address by Dr. J. A. Dulhunty : " Some Items of Geological Interest from Abroad."

September 17th.—Address by Dr. G. D. Osborne and Mr. P. B. Andrews : " Structural Data for the Northern End of the Stroud-Gloucester Trough."

November 19th.—Address by Dr. Leo E. Koch : " Use of the Tetraktys (or System of the Categories of Natural Science) in the Process of Mineral Determination."

In a previous address (Koch, 1948, *a*) the Tetraktys was shown in its application to checking and constructing " schedules " for geological and mineralogical field investigations. In the following address was demonstrated the application of the same system of categories to the whole process of mineral determination.

A critical study into the bulk of the literature on mineral determination published since 1850 revealed that the following four questions, with all their possible mutual combinations and interconnections, are involved in any process of mineral determination :



Answering the complex of these questions in a comprehensive way means to establish a " General Theory of Mineral Determination ". Such a theory, apparently, does not exist at the present time.

The Tetraktys can be applied as a general basis for working out systematically the answers to the questions indicated above. The scheme can also be used for plotting and illustrating all constituent elements, phases, and single procedures of the process of mineral determination.

For example, the order of sequence of the different tests used in each particular table recommended for mineral determination can easily be plotted on " forms " showing the pattern of the Tetraktys, and compared with the order of sequence of any other process of mineral determination.

From the study of more than 70 different tables for mineral determination plotted or represented in this way it becomes evident that, in principle, there is no necessity for following strictly a certain distinct order of sequence of the determinative tests. This fact was already empirically proved by the use of punched cards in the process of mineral identification, first recommended by Gray (1920), worked out by Donnay (1935, 1937, 1938), and modified by Hurlbut (1948).

On the other hand, the Tetraktys can advantageously be used in combination with sets of punched cards ; this latter method makes it possible to avoid a purely mechanical use, or use at random, of the punched cards for the identification of minerals, by directing systematically the determinative process towards such tests and in such an order of sequence as to guarantee a maximum power of discrimination of the tests selected for the determination.

When expressed in the categorical terms of the Tetraktys, the phenomena produced by blowpipe or wet tests prove to be not different in principle from the so-called external or physical characters recommended in certain types of tables for mineral determination. On the other hand, these " dry " tests for minerals prove to have a particularly strong discriminative power in the determinative process of minerals. This is in accordance with the traditional use of blowpipe tests in the most diverse types of tables worked out for the determination of minerals, even in those which are essentially, or exclusively, based on optical phenomena or methods.

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