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Applied Scientific Research: I Did It My Way

E.C. POTTER

PROLOGUE

The Royal Society of New South Wales is incorporated by an 1881 Act of Parliament the preamble to which describes the function of the Society as "the encouragement of studies and investigations in Science, Arts Literature, and Philosophy". Missing from this list are several major callings (such as Law, Medicine, and Divinity), which is just as well since even the most learned men and women of the late nineteenth century recognized their cerebral limitations and specialized.

Of the original 12 Councillors, 7 at least were scientists, and 4 of these were Office Bearers. Thus, from our early days the Society gravitated to Science, but it has always embraced the other three great intellectual pursuits to varying degrees through its Journal, its Library, and public lectures.

In any event few would doubt that Science occupies its own niche in Literature and commands its own brand of Philosophy, and surely the finest advances in Science (but only the finest) display creativity and skill and evoke admiration much as do the greater accomplishments of Art.

SEGMENTATION OF SCIENCE

Science, the objective pursuit and organization of knowledge both in theory and in practice, divides into disciplines by common consent. It hints of career specialization to speak of the disciplines of Physics, Chemistry, and Mathematics, the three bulwarks of many a general science degree.

Within each discipline are its divisions. Thus, to take Chemistry, we have at least Organic, Inorganic, Physical, and Analytical, and there are subdivisions within all of these (like photochemistry and reaction kinetics), each one huge in itself.

But there is a further adjectival specification that can be used to split science, either as a whole or through its disciplines and their divisions. I refer to the two descriptions "pure" and "applied". Thus, we recognize "pure" science (often, but not exclusively, adopted by academics at Universities), and "applied" science (most often associated with technology and industry). Disciplines divide in the same way, for we have pure chemistry and applied chemistry, and more specialized still, pure and applied electrochemistry for example.

In any given instance there is a significant overlap between pure and applied aspects of a scientific discipline, so that mutually exclusive verbal definitions are best not attempted. Some topics are definitely "pure", such as calculating from first principles the degree of separation by electrolysis of the two main isotopes of hydrogen in natural water. The applied version of this topic could well be the large-scale electrolytic production of the much rarer isotopic form, called deuterium oxide or heavy water. Both problems are difficult in their own right, but academics who study and advance the "pure" aspects are (in my experience) much less likely to solve the practical complexities of the "applied" aspects; and vice versa (also in my experience).

Regarding this question of what is "pure" and what is "applied" it is often thought that the "pure" approach attracts those scientists who savour the academic freedom to set their own goals, letting their intellectual enlightenment expand and divide without restraint. In contrast, the "applied" approach would seem more the domain of the practical scientist whose job it is to solve industrial-type problems within unavoidable constraints of time, economics, and materials, to name a few.

Here polarization of viewpoint is the pitfall, but at risk of being a little mischievous, perhaps one may tentatively suggest that, justifiably, the pure scientist is bent on discovery, but is less concerned what is discovered so long as publications accrue, whereas the applied scientist is equally bent on discovery, but it has to be useful and the cheaper, cleaner, and sooner the better.

Well, for better or for worse, I prefer to call myself an applied researcher with a broad scientific base and an eye for a deficiency in fundamentals that has to be remedied if development is to proceed on sound principles and persistent problems are to be overcome. I shall illustrate this theme by referring to the two main areas I have been fortunate to pursue scientifically, namely, keeping boilers intact and clearing smoky chimneys.

My motive is didactic, for I find much applied research is scientifically uninspired, whereas academic research may be clever but is too often unrealistic. I make no apology for the age of the published work I shall describe, because it is still relevant, and furthermore, (as many mature-age researchers keep experiencing) today's researchers habitually skimp on literature reviews and thereby risk either reconfirming existing knowledge or announcing re-invention of the wheel, as it were. There is also the temptation among younger scientists to dismiss the previous generation's work as passé and irrelevant - a lot is, but the gems still sparkle.

KEEPING BOILERS INTACT

When I joined the electric power industry in Britain in 1951 the steam boilers on which the nation's electricity supply depended were being erratically beset by corrosion to perforation of the steel tubes within which the circulating boiler water was being vaporized under pressure. The steam, of course, rotated the turbines that drove the electric generators. Figs 1 and 2 depict examples of the corrosion.

Such are the interdependence and immensity of power-station machinery that a tiny hole caused by the loss of twenty grams or so of steel can suddenly bring to a halt for up to a week perfectly serviceable plant supplying electricity to several hundred thousand people. The public would not notice such an incident because power redistribution and stand-by plant are soon mobilized to maintain the electricity supply.

Nevertheless, with the problem out of control and also rife elsewhere, the then British Electricity Authority trusted me, an untried physical chemist lured into electrochemistry, to recruit a small research team to find some remedy. In the event it took us 10 years to do this, but we were unaware at the time that important fundamental aspects of successfully boiling flowing water in furiously heated steel tubes were so poorly understood. Let me enlarge on this.

Fig. 1. Cut length of a high-pressure boiler tube corroded from the inside (the waterside), showing thick-edged hole about 4 cm long where steel embrittled by hydrogen (corrosion by-product) was violently ejected while boiler was operating.

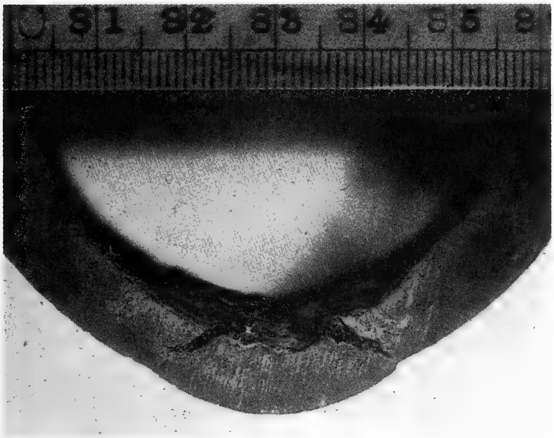

Fig. 2. Part-section through high-pressure boiler tube corroded from the inside almost to failure. The two radial fissures mark the extent of cracking of embrittled metal, but the outside ofthe tube has remained ductile and bulged rather than cracked.

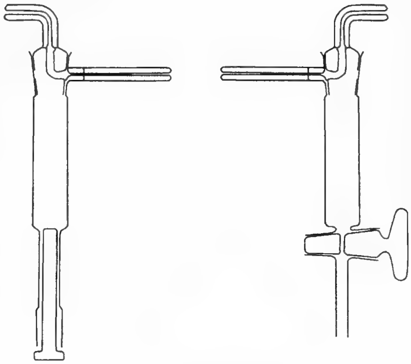

Fig. 3. Alternative designs of glass water sampling vessel allowing small predetermined volumes of liquid reagents to be added successively to the water without any contamination with atmospheric or dissolved oxygen. At 180^{O} to the positions shown for the upper hollow conical closures the calibrated capillary sidearms connect to the vessels' contents via a strap hole (just visible) in the conical sockets.

Dissolved Oxygen the Culprit ?

It's common knowledge that ordinary steel rusts when wetted with water in air. Remove the air initially or subsequently, and the rusting either doesn't start or ceases. This knowledge had long ago rendered routine the continuous deaeration of the feedwater stream to a power-station boiler. However, continuous deaeration is never perfect in practice, and the degree of imperfection was judged by chemically measuring the residual oxygen dissolved in the boiler feedwater. When corrosion continued to be reported despite improved deaeration, the permitted residual oxygen levels were reduced over the years but without the desired effect. By about the early 1950s the residuals being demanded (as low as 1 part in 200 million) were less than the established analytical method could convincingly determine.

Consequently, in an effort to make the analysis more sensitive and reliable, the existing method was dissected and found seriously in error, whereupon it was modified radically, and assessed for precision and accuracy to below 1 part in 10^9. In due course the new equipment and procedure were accepted as the British Standard referee method. Fig. 3 shows the new sampling and reaction vessel, for example.

The analytical upgrade took 2 years, but in the meantime the scientific basis for assigning to minuscule dissolved oxygen levels a significant role in steel corrosion by liquid water in the range 250-350°C was found to be unsound in principle. Anyway, the idea lost credibility every time a fresh corrosion outbreak was reported. After that (but there were experienced applied scientist colleagues who had first to be convinced), the problem and the research programme focused on the basic question: what exactly does happen to steel when it contacts high-temperature water ? The eventual answer, published in 1961, seemed without parallel in the annals of metallic corrosion, and was translated promptly into practical remedial measures that seem to have worked. Let me explain what we found.

A Quart into a Pint Pot ?

It was probably the late Professor Herbert Uhlig of Massachusetts Institute of Technology who first described a steam boiler as a film of magnetite supported by steel, because at all relevant temperatures and pressures massive iron or steel is attacked by air-free water or steam and slowly receives a thin clinging film of the black oxide of iron, magnetite, Fe_30_4, the lodestone of ancient times.

As the magnetite film consolidates and thickens, it progressively impedes its own growth, and after several months its further growth has virtually ceased and the metal stays protected and stable. The quantitative chemical reaction simply reads:

$$3Fe + 4H_20 \longrightarrow Fe_30_4 + 4H_2$$

ie. solid iron + water or steam creates magnetite film + hydrogen gas.

This is all very well, but a straightforward calculation for the conversion to magnetite of (say) the top 10μm of a slab of steel shows that the magnetite produced occupies at least 2.1 times the volume of its parent steel. On a flat surface one can imagine the extra volume being accommodated tidily in free space outside the original surface, but steel in boilers is never flat. It has bends, corners, grooves, and scratches, and, inside a steel tube the magnetite layer curves round on itself creating a situation akin to fitting a quart into a pint pot. So, how can a rigid and breakable film of magnetite manage to protect steel under seemingly prohibitive stress conditions?

Does Protective Magnetite Grow Stress-free ?

To address this problem we carried out replicate oxidation tests using tiny, polished and weighed, blocks of boiler-tube steel immersed in caustic soda solution in small steel cylinders held in a laboratory furnace at controlled temperature in the relevant range. The caustic soda accelerated the magnetite growth, enabling us to get results in a few days. The alkali was also relevant because this and other solutes enrich locally in the boiler water when it boils furiously at the boiler tube surface.

Because a given mass of steel must chemically combine with more than a third of its weight of oxygen for full oxidation to magnetite, we expected that each steel block would increase in weight during testing. However, we found that each block decreased in weight as it oxidized, the full weight discrepancy being mostly shed to the caustic solution as minute octahedral crystals of magnetite. Only some porous clusters of these crystals remained adhering to the outside of the compact hard protective portion of the magnetite (Figs 4 and 5). Measurement of the further loss in weight of each block on converting its protective

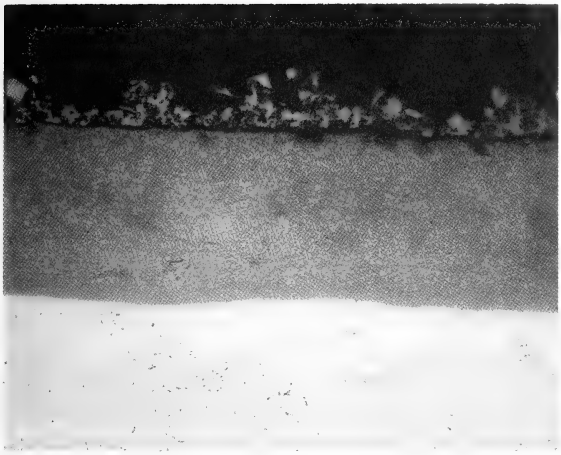

Fig. 4. Section through double layer of magnetite produced by the self-stifling reaction of caustic soda solution on a flat steel surface at 250°C. The irregular layer of coarse crystals is a small part of the non-protective magnetite, and the dense uniform layer bonded to the steel (white) is the protective magnetite occupying the same volume as that of the steel oxidized.

Fig. 5. Top view of the outer non-protective carpet of magnetite octahedra, the dense protective layer being out of sight beneath.

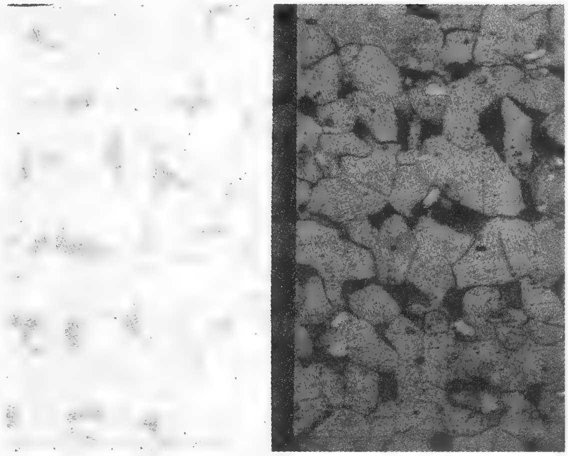

Fig. 6. Top view of the same area of a steel surface before and after magnetite formation. On the left the original polished steel surface has been conventionally etched to show the usual dark pearlite grains of the steel structure. On the right at the same magnification the view is of the protective magnetite formed on that same area of steel. The pearlite grains, still averaging 10 µm in size but now only ghosts have clearly been undisturbed during their oxidation to magnetite, showing that the magnetite layer forms without significant stress.

layer back to its parent steel using pure hot hydrogen gave us the weight of the protective magnetite film.

All the observed weight changes together with the densities of steel and magnetite enabled us to work out that the steel surface received its protective layer of magnetite without significant dimensional change and therefore without the layer being stressed to fracture or dislodgement. Observations using the metallurgical microscope confirmed that grain features of the steel were retained without dimensional distortion on being converted wholly to magnetite (see Fig. 6).

But what happens at a sharp corner? Surely the iron atoms imminently awaiting conversion to magnetite right at the corner have to decide (as it were) which of the three plane faces meeting there they will join, in which case can we not expect the film to gape leaving the corner poorly protected?

Observation under the optical microscope of the protective film at the corners showed its outer surface following the original right-angled profile. The corner echelons of metal atoms clearly had a triple exposure and in their conversion to magnetite a progressive rounding of the steel/magnetite interface was taking place. Thus, film continuity was maintained, as it also was in a steep-sided recess (such as a scratch). Here the outer surface of the magnetite retained the steep-sided profile, but) exposure was clearly hindered and the rounding of the steel/magnetite interface corresponded to a thinner magnetite film than was the case on flat planes (see Figs 7 and 8).

New "pure" knowledge overcame the "applied" problem.

The above description summarizes a long path to understanding, but the excursion of applied science into the fringes of the fundamental realm was exciting and it at once steered our research into uncharted territory through which we foraged at an invigorating pace, doing it my way as it were.

As regards the fine-scale course of the protective film formation, it is evident that this tough magnetite barrier must be porous at some invisible level to have grown at all. If the porosity is at the scale of the ionic crystal lattice of magnetite itself, then its constituent negatively-charged oxide ions (O^{2-}) migrate inwards jumping across the lattice, ensuring the newest part of the growing film is at the metal/magnetite interface. At the same time the electrical equivalent of positive ferrous and ferric ions migrate outwards and contribute the crystallites of magnetite that are shed to the aqueous surroundings at a diminishing rate as the thickening oxide reduces the flux of ions through itself.

As regards the practical outcome of this fundamental foray into oxide film growth, suffice it to say we worked out how to reproduce the boiler-tube corrosion in the labora-

Fig. 7. At a sharp corner the original profile of the steel is retained as protective magnetite, but the acceleration of the oxidation there makes the steel/magnetite interface rounded.

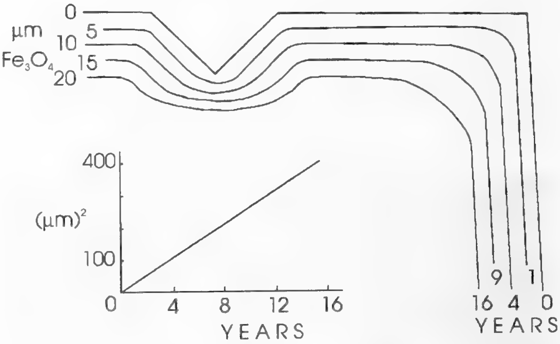

Fig. 8. Theoretical representation of four protective magnetite thicknesses and corresponding successive positions of the magnetite/steel interface during indicated years of oxidation in high-temperature water. The sharp corner (top right) marks the original position of the steel surface before oxidation and shows the local oxidation rate there accelerating to round off the magnetite/steel interface. The V-notch (near top left) represents a surface scratch, which retains its recessed right angle throughout the oxidation, but the oxidation rate is reduced at its deepest part. The inset graph shows that the flat-plane thickness of protective magnetite increases parabolically with the years, indicating the self-stifling mode of growth of the layer.

tory at will, including the dreaded *permanent* embrittlement of as-yet uncorroded steel. By disturbing the finely-balanced ionic countercurrents necessary for protective magnetite growth, we accelerated the corrosion (oxidation) process around one thousand times and produced non-protective magnetite as a consequence, including a gaping unprotected corner.

Several factors, we found, could conspire to induce the corrosion, but a principal one was slow but persistent contamination of the boiler water with traces of particular chlorides unstable at the boiling temperature. Fortunately, all the detrimental factors could be brought under control in ways practicable in the largest power stations, but that is another story.

CLEARING SMOKY CHIMNEYS

I alter course now to describe another forced excursion from the applied to the fundamental that began in 1968 on my being invited by CSIRO to confront a rather different applied problem.

Only a centimetre's journey out through the inner wall of the boiler tubes addressed above, there is the furnace – an enormous enclosed space, blindingly incandescent inside, with fuel burning at 1500°C or more. If the fuel is powdered coal (as is often the case), its combustion generates billions of minute globules of molten siliceous residue that merge and solidify in the flue-gas stream to a greyish glassy dust called pulverized fuel ash (*pfa* for short). The flue gas (essentially moist air much depleted in oxygen and enriched with carbon dioxide) discharges from the power station chimney at about 100 km/h and 100°C, but first it must be cleared of suspended *pfa* to below certain statutory limits, corresponding to near-invisibility of the chimney plume against a cloudy sky.

From the 1920s onward this dust removal was performed by the electrostatic precipitator, a huge steel box through which the hot turbulent flue gas passes at 1 to 2 metres/second, and inside which every suspended particle quickly becomes negatively charged by a high-voltage corona emission. The associated electric field causes the particles to drift transversely on to rows of earthed metal plates, which accumulate ash deposits that are periodically dislodged into hoppers beneath for bulk disposal later.

Sir Oliver Lodge, a renowned physicist, built the first working precipitator in 1883, but without a reliable source of high voltage its performance was poor. With the development of the rotary rectifier the way ahead was clear and in 1907 Frederick Cottrell, an American physical chemist, appeased farmers near San Francisco by using a precipitator to clear a sulphuric acid chimney-plume. From then on, as industrial applications multiplied and air pollution laws tightened, operational limitations and varied problems with electrostatic precipitators came to be recognized.

No scientific fundamentals emerged for the electrostatic precipitator until 1922 when Walther Deutsch published in Germany the equation, named after him, that underpins the technology to this day. Although the deduction of the Deutsch equation is straightforward and sound, it will not be repeated here but rather justified using persuasive description.

The Deutsch Equation

Consider a plain vertical tube 20 cm in diameter (say) and about 2 m. high. The tube is earthed electrically and has a high-voltage wire centrally (Fig. 9). A turbulent stream of dust-laden air enters at the bottom, and the then electrified rising particles veer towards the tube wall and stick

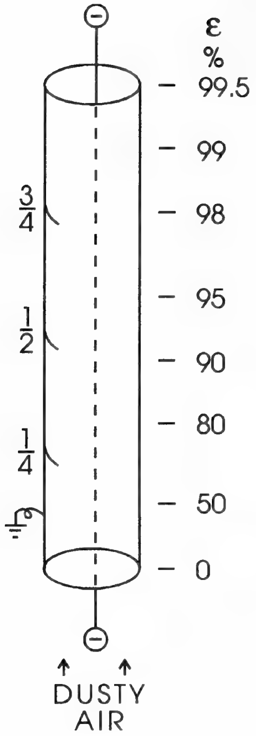

Fig. 9. Representation of tubular electrostatic precipitator removing dust from rising air stream at constant applied voltage. The right-hand vertical scale conforms to the Deutsch equation and gives the collection efficiency, ε, at any selected height in the tube, up to the value 99.5% at the tube outlet on this occasion.

there. Each parcel of rising air has only a few seconds residence in the tube, making it a race against time to extract as many particles as possible before they reach the top. Nevertheless, the escaping air is visibly much less dusty (say 99.5% less so) than it was originally.

At the bottom of the tube the suspended dust is at its most prolific, and the fastest extraction occurs there. A little thought will persuade the reader that the dust extraction rate at any higher position in the tube depends directly on the remaining dust concentration at that position. This means that in general the dust extraction rate is not *pro rata* on height up the tube, but diminishes more rapidly than this as the partially-cleared gas ascends. Indeed, in a precipitator maintaining 99.5% efficiency, over 82% of the dust has been caught in the first third of the tube. At the tube top the remaining particles are proving elusive, so that the dust extraction rate is minimal and inevitably some particles escape.

Now, if one were to halve the throughput of the air, there would be double the time for dust deposition and the emitted air would be measurably clearer. The same degree of enhanced dust removal (and air clarity also) would be achieved if one maintained the original throughput but doubled the tube length, thus doubling the collecting surface area.

Evidently, there would be a quotient that allows for the reciprocity between these two variables, and this is the collecting area (A, in square metres) divided by the air throughput (Q, in cubic metres per second). That quotient (A/Q, more conveniently replaced by the single symbol α) has long been called the Specific Collecting Area of the precipitator. It is in practice a parameter fixing in a given instance the precipitator size that offers a required or nominated efficiency of dust removal.

The efficiency (ε, a fraction between 0 and 1) is measurable, being the difference between one and the ratio of outlet to inlet dust burdens in the carrier gas (air in the present example). The efficiency ε can also be expressed as a percentage. In practice, efficiencies of 99.5% are common, and 99.9% is far from rare, the size parameter a typically being 60-90 m^2/m^3s^{-1}.

Deutsch's equation reads:

$$\text{Log}\,(1 - g) = -\alpha w/2.303,$$

where the divisor 2.303 is the usual factor to change the base of the logarithm from the natural value 'e' to the common one of 10. The quantity 'w' turns out to be the average transverse speed (or migration velocity, around 5-15 cm/sec) at which the charged suspended particles move across to the collecting surface (the tube wall in this example).

The promise of the Deutsch equation as a principled basis for sizing precipitators for a specified performance was immediately realised in 1922, especially since Anderson, an American engineer, had 3 years earlier seen the logarithmic behaviour in actual practice. As experience grew, however, so did the doubts, because engineers began finding that their Deutsch-based sizing estimates did not always produce a precipitator satisfying the user's or statutory requirements.

As a result, precipitator manufacturers understandably began to espouse the empirical approach, building up from previous experiences (good and bad) their own confidential data banks of so-called 'effective' migration velocities (symbol w_e) calculated from the very Deutsch equation they mistrusted. In this way they expected to reduce sizing errors, which had (more often than not) caused them to build precipitators too small for the job.

By the mid-1960s, sizing mistakes, some large and costly, were still coming to light especially for coal-fired power stations, and the empiricism was being supplemented or even displaced by a totally-practical approach using portable precipitators for pre-design testing of a representative sidestream of dust and carrier gas at the user's premises. However, the problem often was the formulation of the test programme, bearing in mind the constraints of time, cost, and intrusion into the working facility. Further, with the fundamental background so limited, the assessment and interpretation of performance data so as to obtain the most reliable sizing decisions was itself a matter of worrying doubt.

By 1968 it was all too clear that the science of electrostatic precipitation had been neglected in at least the context of factors determining the precipitator performance, and this aspect was the first addressed when the CSIRO research programme was realigned later that year. At the outset the focus was on the Deutsch equation.

The Extension of the Deutsch Equation

To the writer the striking feature of the 1922 Deutsch equation was that the migration velocity was left without scientific elaboration. This is all the more surprising because, in the aftermath of the discovery of the electron in 1897, physicists and later electrochemists had established the basic theory of forces on charged particles and had combined it with Stokes Law of 1850 to formulate the equilibrium motion of such particles in a medium such as a liquid or a gas. Repeated success had accompanied application of various versions of the theory for specific situations.

It was therefore going to be little more than a formality to follow the already established procedure and analyse Deutsch's 'w' The writer could have done it himself in 1947, but electrochemistry beckoned him - and besides, at that time he had never even heard of an electrostatic precipitator!

Be that as it may, by 1956 the British experts on particle dynamics, Rose and Wood, had published their excellent book, including the anticipated formula for 'w'. However, these authors also pointed out that their published formula yielded 'w' values up to double the 'effective' values calculated from the 1922 Deutsch equation using data from certain full-scale precipitators. It seems that this numerical discrepancy was deemed crucial and sufficient in principle to discredit the Rose and Wood theoretical equation, whereas there had been no certainty that the precipitators in question were capable of making a valid test of the theoretical equation.

On entering the scene in 1968, the writer rejected this collapse of confidence in the Rose and Wood equation and did what seemed obvious - he substituted it for 'w' in the 1922 Deutsch equation. After a few acceptable simplifying assumptions for the practical case, the result was:

$$\text{Log}\,(1 - \varepsilon) = Cd\alpha V^2,$$

where C is a constant theoretically known but not usually evaluated, d is particle size (expressed usually as mass median diameter), and V is the voltage applied to the precipitator. The equation showed the overbearing importance of voltage to precipitator efficiency, and placed the influence of particle size into fitting perspective. In practice the applied voltage is limited by the electrical breakdown (seen as flashover or sparking) of the carrier gas or of the dust layer deposited from it.

Later that year when experimental access to a precipitator was gained, it emerged that ε is far from zero when the voltage is off. To accommodate this hitherto unknown fact the equation was formally modified to:

$$\text{Log}\,(1 - \varepsilon) = \text{Log}\,(1 - \varepsilon_0) + Cd\alpha V^2,$$

where ε_0 is the so-called mechanical collection efficiency (typically 0.2 - 0.4) i.e. 20-40%). The introduction of this detail provided a simple graphical explanation for the frequent finding that w_e varies with α, showing it was no more than an artefact and not (as was thought) a reason for rejecting the validity of the Deutsch equation.

This new equation was called the Extended Deutsch Equation, and inspection of it showed that for a given situation plotting the observed values of log $(1-\varepsilon)$ vertically against the corresponding selected values of the product αV^2 horizontally should yield a straight line graph, certainly at efficiencies above so. We soon confirmed this was so, eventually over a large range of particulates, scales of operation, carrier-gas compositions, dust burdens, and temperature.

This kind of graph, novel to the technology, was called the Performance Line, and was specific to a precipitator under the operational conditions imposed or pertaining. The Performance Line provided a convincing, flexible, and precise way of estimating the size that a projected precipitator needed to be for any stated efficiency. It proved to be especially effective for *pfa* from unfamiliar coals, and took the long-standing guesswork and error out of sizing power-station precipitators (see Figs 10 and 11).

The Performance Line also became a valuable diagnostic tool in research. For example, it gave the clue to the way that certain trace flue-gas additives could dramatically improve collection efficiency, namely, by clustering particles to generate a larger effective particle size and by raising the maximum operating voltage.

EPILOGUE

The opening theme of this Address contrasted the two major categories of Science, "pure" and "applied". The theme was then developed by exemplifying ways in which one committed applied scientist had been prepared to rectify perceived gaps and weaknesses in fundamental principles.

In conclusion I offer the following proposition for debate: that applied science is alive but unwell. Too often, it seems to me,

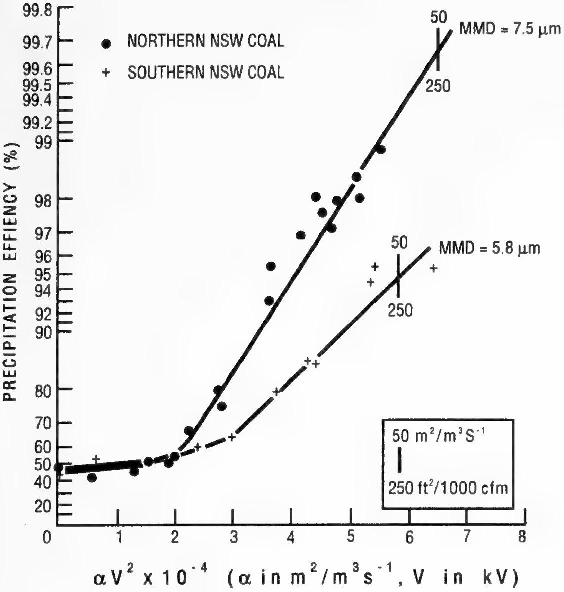

Fig. 10. 120°C data from the same precipitator for two Eastern Australiancoals (each 0.4% sulphur) illustrating slope of Performance Line responding to particle size of *pfa* (as mass median diameter, MMD) in accord with Extended Deutsch Equation. Short vertical bars on the Performance Lines indicate respective highest efficiencies attainable at α = 50 and with voltage at maximum. The finer ash is collected much less efficiently.

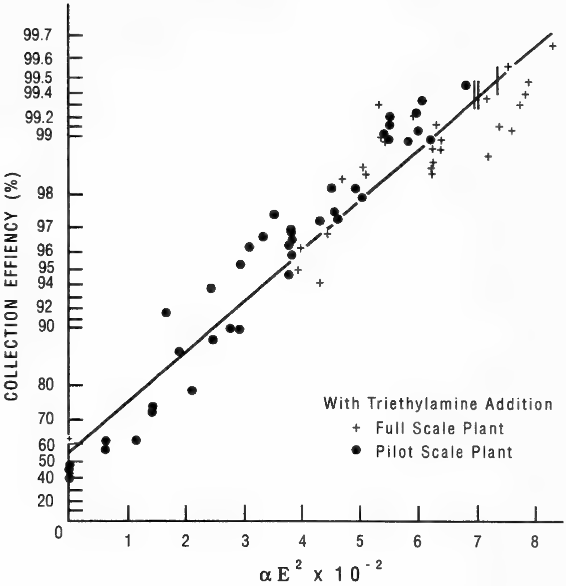

Fig. 11. Illustrating that the same Performance Line for a *pfa* from the same coal (0.4% sulphur) is obtained from different precipitators when the applied voltage is transformed into the corresponding average electric field (E) on dividing by the respective wire-to-collector plate distance. The single vertical bar is for the full-scale plant at 210°C and $\alpha = 60$ m^2/m^{3}s^{-1} at maximum field (i.e. voltage), and the double bar is for the pilot plant under the same operating conditions.

important applied problems are losing out on solution because the fundamental science either has crucial gaps in it or needs alignment away from the esoteric to the more immediately useful. The debate could address whether it is for applied scientists to tell their academic counterparts where the gaps are, or whether the pure scientists should devote time for dialogue with the reserved world of industrial science. Perhaps even, we should contemplate reforming scientific teaching and education so that, in time, the nation's research and development fall more into the hands of scientists demonstrably dedicated to the communally-rewarding use of our cerebral resources.

FURTHER READING

This Address is not a research paper of the familiar kind requiring references to every step in the argument and its development. Rather is this document a condensed narrative of two long research journeys, either of which could encourage further reading selected from the following lists.

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7. ACKNOWLEDGEMENTS

The author is indebted to his supervisors for constant encouragement and support during major stages of the researches covered here, namely the late Mr.R.Ll. Rees, the late Mr I.E. Newnham, the late Dr D.F.A. Koch, and Mr A.V. Bradshaw. The author thanks also the numerous members of his research teams for their valuable and dexterous work, and wishes to single out especially Mr G.M.W. (Geoff) Mann, Mr J.F. (Fraser) White, and Mr C.A.J. (Colin) Paulson, all of whom made meritorious and sustained contributions to specific advances described above. There were several other team members who equally deserve accolades for their superb work, but space could not be found here for adequate coverage of their efforts.

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Presidential Address delivered before the Royal Sosciety of New South Wales on 1st April 1998.

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Maldonite and Its Paragenesis at Kingsgate, New South Wales

L.J. LAWRENCE, A.R. RAMSDEN & VERA MUNRO-SMITH

ABSTRACT. The occurrence of maldonite (Au_2Bi) in the molybdenite-bismuth quartz pipes of Kingsgate, in the New England region of New South Wales is described. This intermetallic compound is present as minute particles embedded in gold inclusions in native bismuth, with associated bismuth telluro-sulphides. Evidence that maldonite may be the product of solid-state diffusion between gold and bismuth is indicated where maldonite forms a reaction rim around corroded particles of gold embedded in bismuth. Rare myrmekitic intergrowths of gold and bismuth are considered to be breakdown products of metastable maldonite. Joseite (Bi_4TeS_2) and Joseite-B (Bi_4Te_2S) are the principal associated bismuth tellurosulphides, accompanied by a possibly new bismuth telluro-sulphide mineral ($Bi_{10}Te_2S_5$).

INTRODUCTION

Maldonite, Au_2Bi, is a relatively rare intermetallic mineral belonging to the cubic system and space group Fd3m. The mineral was originally found in the Nuggety and the Union gold-bearing quartz reefs at Maldon in central Victoria. Maldonite is bright silvery in colour with a faint pinkish overtone, it eventually tarnishes to brown and ultimately to a blackish colour, whereupon it became known to the miners as "black gold".

The mineral was named maldonite by Ulrich in 1870 and further characterised by him in 1875. Controversy ensued because the existence of a compound Au_2Bi was considered extremely doubtful since it was impossible to produce it experimentally from a melt of gold and bismuth. The matter was eventually resolved when the mineral was synthesised by solid-state diffusion as outlined by Edwards (1960); a natural example of this diffusion reaction is documented in this paper, along with other aspects of paragenesis.

Fig. 1. Map showing the location of Kingsgate.

TABLE 1
PRIMARY MINERALS OF THE KINGSGATE MOLYBDENITE PIPES
(After Lawrence and Markham 1962, with later additions)

Major components	
Molybdenite	MoS_2
Bismuth	Bi
Bismuthinite	Bi_2S_3
Minor components	
Pyrrhotite	$Fe_{1-x}S$
Pyrite	FeS_2
Chalcopyrite	$CuFeS_2$
Ikunolite	Bi_4S_3
Arsenopyrite	FeAsS
Joseite	Bi_4TeS_2
Joseite-B	$Bi_4(Te,S,Se)_{3-x}$
Unnamed phase	$Bi_{10}Te_2S_5$
Gold	Au (± Ag)
Tetradymite	Bi_2Te_2S
Cassiterite	SnO_2
Wolframite	$FeMnWO_4$
Galenobismutite	$PbBi_2S_4$
Cosalite	$Pb_2Bi_2S_5$
Accesssory components	
Galena	PbS
Sphalerite	ZnS
Pyrargyrite	Ag_3SbS_3
Maldonite	Au_2Bi

For some time maldonite was thought to be a mineral unique to the gold deposits of Maldon, but with the advent of the electron microprobe, numerous other occurrences have been recorded. It has been found in hydrothermal deposits at Cobar and at Rockley in New South Wales, in skarn at Nevoria near Southern Cross, Western Australia and in the Challenger Prospect in the Gawler Ranges, South Australia. Overseas, maldonite has been observed in ore from Akjoujt, Mauritania; in skarn from Rezbanya; from Ingham, Ontario, Canada; as a myrmekitic intergrowth in bismuth from Ishibashi, Japan; from Tyrnyauz and Transbaikalia, Russia; in hydrothermal veins at Zarmitan, Uzbekistan; in veins from Mokksrsko, Czec Republic; from Sierra County, New Mexico; in the Bushveld Complex, South Africa; and in hydrothermal veins in the Salsigne and Scoufour Cantal gold deposits in France. However, except at

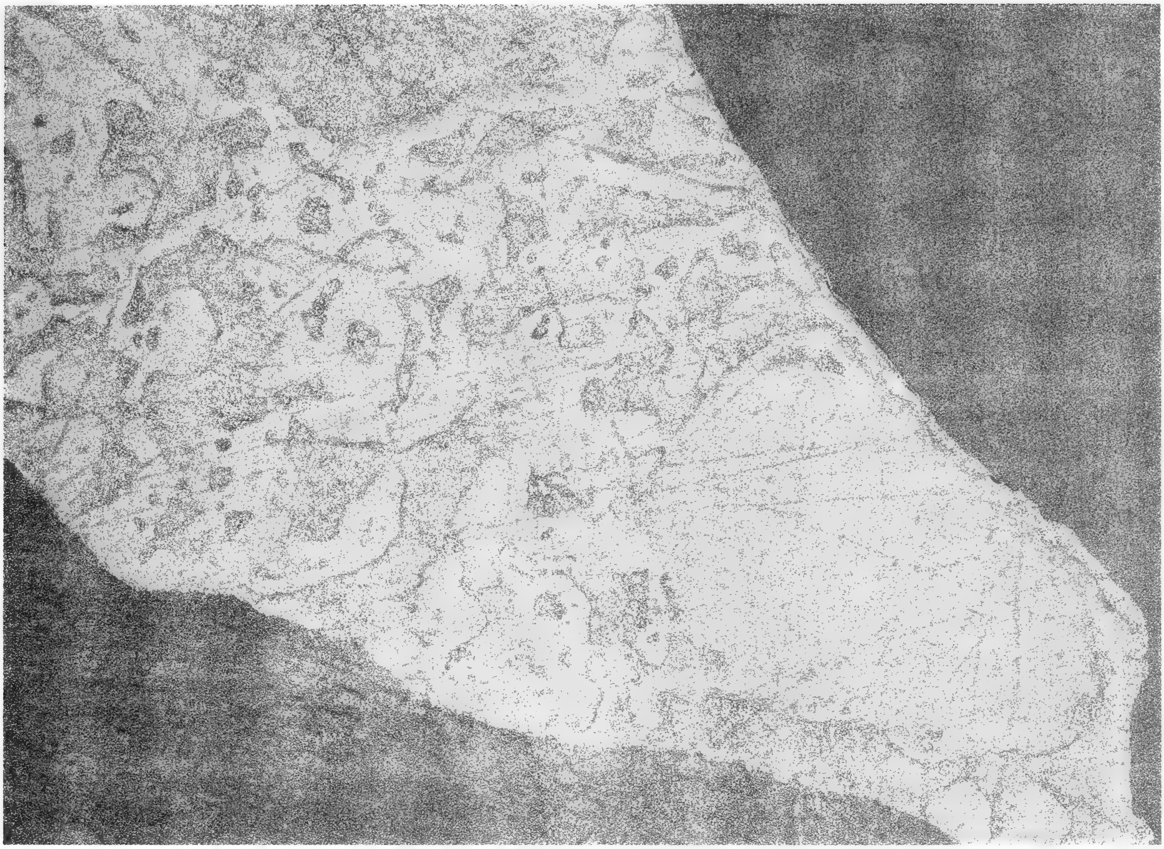

Fig. 2. Reaction rim of maldonite (light grey) surrounding and filling corrosion voids in gold in an outer bismuth matrix which has reacted with the gold by solid-state diffusion. Reflected light photomicrograph, phase contrast enhanced electronically. Area of specimen shown 1.5 mm x 1.0 mm.

Maldon, where centimetre-size pieces of unaltered or tarnished maldonite ("black gold:) were obtained, all other occurrences to date are of microscopic dimension.

MICROPROBE ANALYSIS

The presence of maldonite at Kingsgate, albeit as an accessory component of a complex multimineralic ore, dominated by molybdenite and bismuth, is here confirmed by electron microprobe analysis.

The Kingsgate mining field is situated 30 km east-south-east of Glen Innes in the northern New England region of New South Wales (Fig. 1). The mines were significant producers of molybdenite and bismuth which occurred in pipe-shaped masses of lode quartz emanating from a silexite differentiate within a highly acidic granite (SiO_2 77.60%) of epi-Permian age. The deposits are of high temperature type with eventual development of some lower temperature minerals such as pyrargyrite, albeit in trace amounts. The mineralogy of the Kingsgate deposits is given in Table 1 (after Lawrence and Markham 1962).

A further study of polished sections of native bismuth from Kingsgate revealed the presence of numerous grains of gold as inclusions in the bismuth. The gold grains

TABLE 2
ELECTRON MICROPROBE ANALYSES OF MALDONITE AND ASSOCIATED ORE MINERALS

	Bismuth	Gold		Maldonite	Joseite-B	Unknown	Chalcopyrite	Pyyrhotite
					(wt%)			
		(a)	(b)					
Bi	100.7	<0.1	<0.1	32.4	75.8	83.0	0.2	0.1
Au	<0.1	94.7	98.8	67.1	<0.1	0.2	0.1	0.1
Ag	na	4.1	0.4	na	na	na	na	na
Fe	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	29.3	60.1
Cu	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	33.5	<0.1
Te	<0.1	<0.1	<0.1	<0.1	21.0	10.2	<0.1	<0.1
S	<0.1	<0.1	<0.1	<0.1	2.8	6.7	35.4	39.8
TOTAL	100.7	98.8	99.2	99.5	99.6	100.1	98.5	100.1

Note: (a) = Ovoid gold inclusions in bismuth; (b) = Myrmekitic gold with maldonite.
na = not analysed.

are often crudely ovoid in shape and from 0.05 mm to 1.75 mm long. Electron microprobe analyses in the present study show that they contain about 4 wt%Ag (Table 2). In addition to the gold, irregular shaped inclusions of joseite (Bi_4TeS_2) and, less commonly, joseite-B (with an analysed composition Bi_4Te_2S) occur in some of the bismuth specimens.

The larger of the gold grains are surrounded by a rim of another (unidentified) mineral. The polishing hardness of this mineral is slightly less than for gold (H 2.5 - 3), but similar to that of the bismuth matrix (H 2 - 2.5). The unidentified mineral (Fig. 2) has a high reflectivity, about the same as for bismuth, appears creamy white with a bluish-green overtone in plane-polarised reflected light, and is isotropic, and therefore cubic. The same mineral was observed as minute inclusions in gold within bismuth.

Electron microprobe analyses (Table 2) confirm that the previously unidentified mineral is maldonite. The associated minerals are bismuth, gold, chalcopyrite, pyrrhotite, joseite-B, and an unknown bismuth telluro-sulphide having a formula $Bi_{10}Te_2S_5$. This latter phase is apparently a new mineral and is currently being investigated in more detail.

The reaction rim texture of Fig. 2 clearly indicates that maldonite at Kingsgate has formed by solid-state diffusion reaction between gold and bismuth, although occasionally gold has been observed in contact with bismuth, embedded in molybdenite, without any sign of reaction between the two phases (Lawrence and Markham, 1962).

Detailed electron microprobe investigation of a myrmekitic intergrowth of gold and bismuth (Fig. 3) revealed a few minute (<10 μm) inclusions of maldonite within the gold (Fig. 4). The composition of the myrmekitic gold is essentially pure (Table 2), in marked contrast to the argentian composition of the ovoid inclusions described above. The myrmekitic texture is interpreted as the break down of maldonite into its elemental components and the inclu-

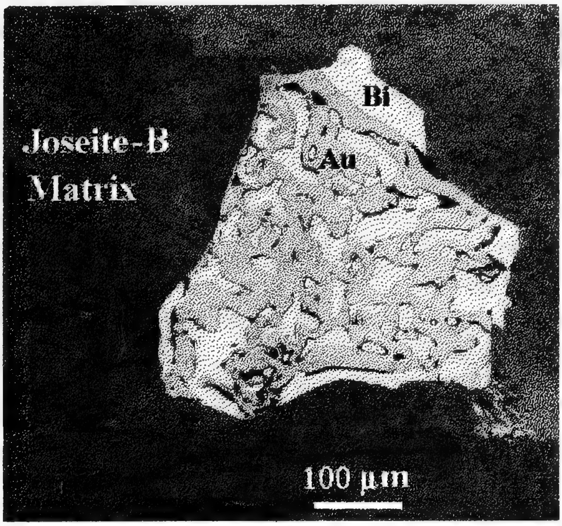

Fig. 3. Myrmekitic intergrowth of bismuth (white) and gold (light grey) embedded in joseite-B (dark grey). The texture is interpreted to result from breakdown of a particle of maldonite into its elemental components. Minute inclusions of relic maldonite occur in the gold (see Fig. 4). Backscatter electron image. Scale bar = 100 µm.

sions are interpreted as relic maldonite. Element concentration profiles for gold and bismuth across one maldonite inclusion (Fig. 5) show very sharp contacts between the maldonite and gold, consistent with this interpretation.

The results of this microprobe study suggest, further, that maldonite is a metastable compound, which may form or decompose depending upon the prevailing physicochemical environment:

$$2Au + Bi \rightleftarrows Au_2Bi.$$

CONCLUSION

The co-existence of maldonite both as reaction rims between gold and bismuth and as relic inclusions in gold-bismuth decomposi-

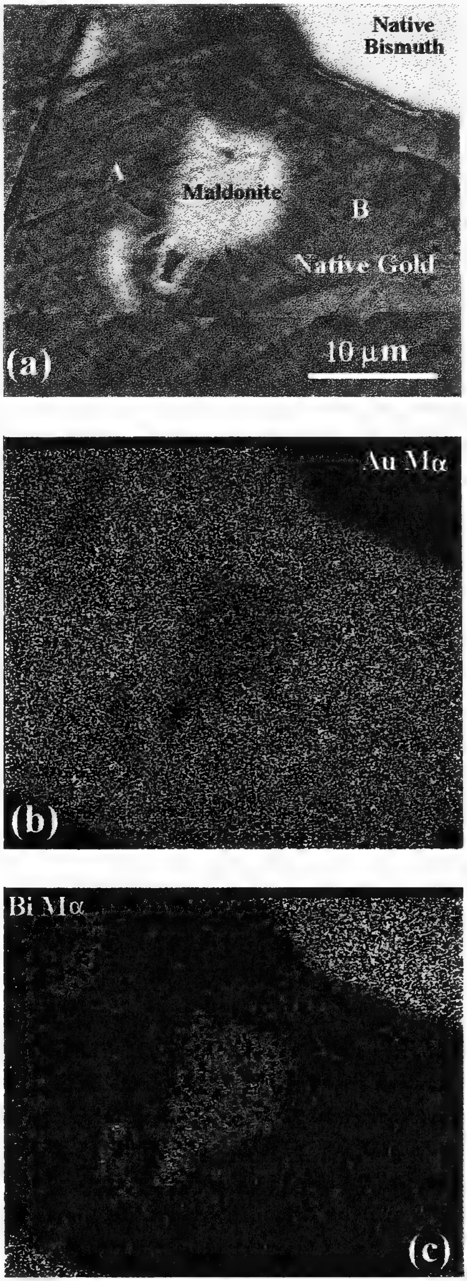

Fig. 4. Maldonite in a particle of myrmekitic gold and bismuth. (a) Backscatter electron image showing relic inclusion of maldonite (mid-grey) in gold (dark grey) with bismuth (white). Locations A and B. mark the start and end points of an electron beam line scan across the inclusion (see Fig. 5). Scale bar = 10 µm. (b) Element distribution map for gold (Au Mα X-rays). (c) Element distribution map for bismuth (Bi Mα X-rays).

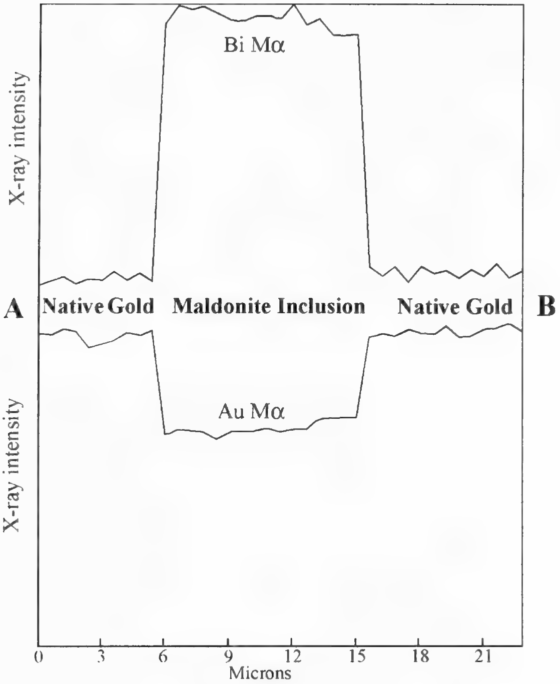

Fig. 5. X-ray intensity profiles for Au Mα and Bi Mα across the maldonite inclusion shown in Fig. 4 (line A - B). Note the sharp contacts between the maldonite and gold.

tion products suggests that conditions during formation of the Kingsgate bismuth-rich ores fluctuated close to the stability field for maldonite. As the ore fluids cooled, formation of maldonite would be favoured where short lived temperature increases resulted in atomic diffusion reaction between gold and bismuth, while decomposition of maldonite into gold and bismuth would be favoured where there was a slightly accelerated drop in temperature.

The occurrence of maldonite at Kingsgate differs from other recorded localities in respect to its paragenetic relationships: as reaction rims around and within myrmekitic gold grains, as particles of original maldonite embedded in the gold and as small decomposed grains seen now as myrmekitic intergrowths of gold and bismuth. The study further attests to the metastable nature of maldonite.

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Then Look Not Coldly on Science. Joseph Campbell, M.A. Journeyman Cleric

DAVID BRANAGAN

ABSTRACT. The name of the Reverend Joseph Campbell (1856-1933) is virtually unknown today. However, he was one of the most brilliant of the early graduates of the University of Sydney. A man of restless energy, he worked particularly in Eastern Australia and New Zealand, devoting himself to many areas of applied science, in particular technical education, ore treatment and crop development over a period of more than forty years. One of Campbell's books on practical geology went through numerous editions and reprints between 1885 and 1931. He was particularly interested in the relations between Science and Religion, and developed his ideas in a number of publications. However, his wide interests and criticisms offended some Anglican bishops. While his successful agricultural work in North Queensland is recognised locally, his apparent increasing eccentricity caused him to be ignored by scientists in his later years and he died virtually forgotten. There are probably numerous forgotten "Campbells" in the history of Australian science and technology who deserve to be studied and honoured for their contributions.

CLERIC IN TRANSIT

The Reverend Joseph Campbell was born at South Creek, St Mary's, west of Sydney on 13 September 1856. The son of William Branch and Elizabeth Anne Campbell (née Jackson), who came to Australia in the late 1840s and "entered into pastoral and subsequently commercial pursuits", Campbell "spent his early years at the beautiful old home, 'Clarence Villa,' on the heights overlooking the Lane Cove River" and apparently attended private schools. Then he lived for some time on his "father's fertile estate, known as 'Fountain Dale', Kiama" and, under the guidance of his private tutor, "studied the principles of agriculture on the farm, and engineering in the fitting room of a mill on the estate". He matriculated in 1877, but for several years previously was a schoolteacher at another family property, 'Flushcombe', near Prospect west of Sydney (Campbell 1922).

Joseph Campbell had a long career in the Church of England, although originally baptised as a Presbyterian. While attending the University of Sydney, he held a St Paul's College Fellows' Scholarship between 1877 and 1880, studying Divinity. At St Andrew's Cathedral, Sydney, Campbell was ordained Deacon by the Bishop of Sydney on 21 December 1880 and on 21 June 1882 was ordained Priest for the diocese of Sydney by the Bishop of Bathurst (there being no Bishop of Sydney at the time, Bishop Barker having died in April). He was assistant and curate at St Michael's, Surry Hills, 1881-3, living at 'Edgarville', Botany Road, and at 'Somerset House', Surry Hills (1882).

Campbell became incumbent at Holy Trinity, Glen Innes, in 1883, remaining until 1889 (although there was a long period of leave), was *Locum Tenens* of St Jude's, Randwick, October 1889 - October 1890 and then became assistant minister of St Nicolas, Coogee until August 1891, when it was still attached to St Jude's. From August 1891 to 1897, Campbell was "Minister in the mission district of St Nicolas", the incumbent earning £150. He was also Principal (Professor) of St Nicolas' College, Randwick, between 1893 and 1897 and a Fellow of St Paul's College, University of Sydney, from 1895 to 1897 (*Sydney Diocesan Directory* 1896).

Between 1897 and 1900 Campbell (Fig. 1) held a general licence in the Diocese of Auckland, New Zealand, being Acting Vicar of St Sepulchre's "during the absence of the incumbent". He was *Locum Tenens* at St Paul's, Papanui, near Christchurch, from 29 September 1900 to 13 March 1901, before being appointed vicar until 1 December 1903. His departure date from Christchurch was actually in November (*Australian Mining Standard* 26/11/1903). He returned to Australia to become Archdeacon and Rector of Cairns, North Queensland, from 1904 to 1909, resigning in September at the age of fifty-three, just after he departed for an overseas visit in connection with his research on cotton (*Cairns Post* 30/9/1909; Crockford 1916). Although Bishop Frodsham remained personally friendly and urged Campbell to reconsider, the Bishop did not approve of his "relinquishing his spiritual duties for material interests" and issued a caveat upon him in 1910 (i.e. a formal warning to other bishops to contact him prior to offering Campbell an appointment). Campbell remarked several times that much of his church work was, in fact, carried out on an "honorary basis". Campbell returned to North Queensland from Europe, probably in 1912, and settled at 'Gossypium Park', Kamma, a few kilometres south of Cairns.

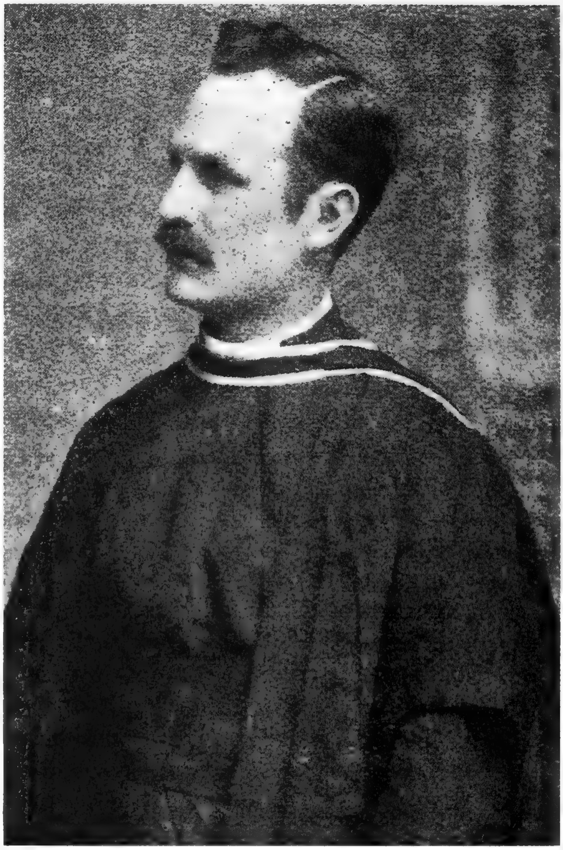


Fig. 1. Rev. Joseph Campbell, M.A.

In 1882 Campbell married Eliza Marion Holt (daughter of William Holt of Parramatta), "double prize woman and medallist in French at the junior and senior university exams" and of "independent means and was thus able to further prosecute my honorary scientific work" (*Australian Mining Standard* 15/7/1897). There were two children of the union, but his wife died in London on 24 October 1901, aged 40, while their two daughters were finishing their education in France and England. The daughters were living in New Zealand in the 1920s, although they had joined him in Cairns in 1904 (Campbell 1922).

Campbell remarried late in 1909 (probably in Sydney) "one of the noblest and most stately young ladies of North Queensland, of distinguished Scottish descent on her mother's side, and good old English yeoman farmer's descent on her father's side. By her I have three children, viz., two girls (Nellie and Ella) and a boy, named Cadmus, [b. probably 1919] after the great Grecian warrior and Prince, who introduced the Greek alphabet into Greece" (Campbell 1922).

SCIENTIFIC INTERESTS

One would have thought these activities should have been enough to keep Campbell busy. However, there was another side to Campbell, hinted at by the F.G.S., F.C.I. and other letters, which appear after his name in various publications, and by his course of study for the B.A. degree. Campbell is reported as taking "Holy orders .... but with the firm intention of devoting much of his time to scientific work after the example of the late Revs. W.B. Clarke and J. Tennyson [sic] Woods, of New South Wales" (*Australian Mining Standard* 15/7/1897). Campbell's interests in science could have been encouraged during his years at St Paul's College by the Wardens at that time. Rev. William Scott, Warden to 1878, had formerly been the Government Astronomer; and he was followed by Rev. W. Hey Sharp, a chemist. The Bishop of Christchurch during Campbell's time there was Churchill Julius, who had an interest in engineering and science. Julius's son, Sir George Julius, became a prominent engineer in Australia, acting as Chairman of C.S.I.R. from its formation in 1926.

Campbell (Fig. 1) graduated Bachelor of Arts from the University of Sydney in June 1880 and took the Master of Arts degree two years later. In his Bachelor's course he studied mathematics and natural science, gaining the Belmore Scholarship for proficiency in geology and agricultural chemistry. His Bachelor's results apparently led to his being offered a position at the Ballarat School of Mines, which he declined "as he wished to devote some time to the study of theology, which he had always regarded as the highest branch of science, requiring an extensive knowledge of other branches to unfold its mysteries" (*Australian Mining Standard* 15/7/1897). However, during Professor John Smith's absence on leave from Sydney University in 1882-3 Campbell was appointed Acting Professor.

Campbell was elected a Fellow of the Geological Society of London in December 1886, but was 'removed' on 27 June 1900 (probably for non-payment of his subscription). About the same time (1886) he was elected to the Linnean Society of London, and was also for a while a Fellow of the Chemical Institute. At the time of his election to the Geological Society he was living in Glen Innes, where, according to the Society, his address remained until 1891, so they probably had trouble keeping up with his various moves. He was later elected a member of several other scientific and technical bodies, including the Federated Institute of Mining Engineers, England, but his opportunities for direct participation were obviously limited and he seems to have gradually shed these memberships and fellowships, although he referred to them in his 1922 publication, but not in his 1923 paper, where M.A. holds sway from both Sydney and New Zealand, the latter having been awarded *ad eundem gradum* in 1903.

CAMPBELL, THE WRITER

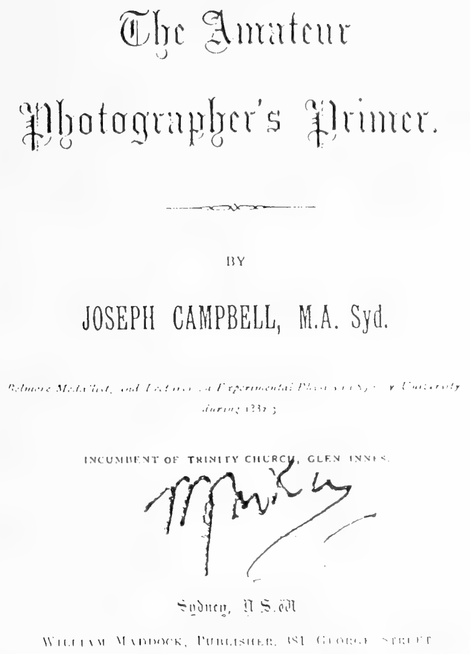
From an early age Campbell regarded himself as a teacher and part of this attitude was the preparation of suitable reading material, though there was clearly an element of self-advertisement in this work. His first book (perhaps better called a booklet, 8vo, 80 pages) appeared early in 1876, before his twentieth birthday. *The Physical and Political Geography of Australia, Tasmania and New Zealand* was essentially a compendium of facts about the Australasian colonies. It listed counties, towns, rivers and mountains, and gave information about the form of government in each colony – all in all a useful document for the rote learning that was a feature of most education at the time. Although the 1897 interview (*Australian Mining Standard* 15/7/1897) states that these "literary labours were given to the world .... after extensive travel in the colonies", there is no evidence in the text that Campbell based the data on his own experiences, and the preface indicates that the booklet was just the enthusiastic gathering of facts from different sources to provide information in a reasonably-priced form for both teachers and students. That it was an immediate success is demonstrated by the printing of a second edition the same year, but by a different Sydney publisher.

Campbell's next publication was another booklet, this time only thirty pages, *Norfolk Island and its Inhabitants*, which appeared three years later (March 1879, St Paul's College) and again with a new Sydney publisher, Joseph Cook, who was then the official publisher for the Church of England in Sydney. This booklet was a product of Campbell's own experience, as he had been contemplating offering himself for the Melanesian mission. He spent three weeks on the island learning something about the inhabitants. He claimed that he checked with the elders and leaders everything he had been told and written and so offered it with some confidence. However, his brief sojourn there apparently convinced him that mission life was not for him. There is some fine writing in this pamphlet about Norfolk Island, "one of the happiest spots on earth". Campbell was to go on and publish a number of other pamphlets, but of a more specialised nature.

JOSEPH CAMPBELL - PHOTOGRAPHER FROM 1884

Campbell early realized the value of photography as a didactic tool, as well as an art form, and that there was an intellectual stimulus in making decisions about the choices of the best site and conditions for any particular photograph. By the early 1880s he had become a competent photographer, carrying out all steps from photo to print. In 1884 he prepared and published a small but very practical booklet *The Amateur Photographer's Primer* (Fig. 2), noting that it contained basic information only, and recommending other, more technical, books for further instruction. His booklet contained a list of necessary apparatus, with costs, the material being obtained at "Mr. Cargill's Photographic Stock Department, 28 Market Street [Sydney]."

Campbell's pamphlet "*Gold & How to Get it*", the text of a lecture given on December 3rd 1894, contained three photos, the cover showing prospectors in the field (Fig. 3). Campbell noted, in the text, with regret, his inability to reproduce his many lantern slides but "two of them are of such importance that an exception must be made in their favour". The two were related to the ore treatment being used at the Cangai Mine, Clarence River (see Fig. 7). Mitchell



The Amateur
Photographer's Primer.

BY

JOSEPH CAMPBELL, M.A. Syd.

Belmore Medallist, and Lecturer in Experimental Physics [illegible] University
during [illegible]

INCUMBENT OF TRINITY CHURCH, GLEN INNES.

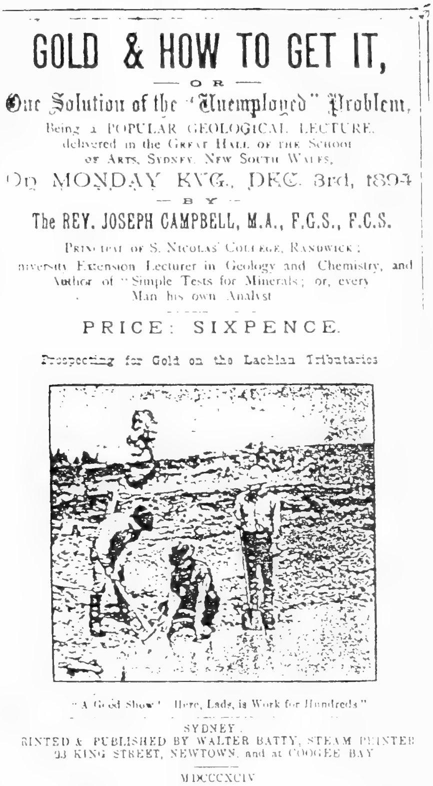
Sydney, N.S.W.

WILLIAM MADDOCK, PUBLISHER, 181 GEORGE STREET

Fig. 2. *The Amateur Photographer's Primer.*

Library Photography Curator, Alan Davies (pers. comm.) notes Campbell's competence in these difficult indoor photos. Press notices of this lecture report it as being "illustrated by graphic limelight views" and a "large number of excellent photographs" and the text itself was interspersed with several indications of their use: "here followed a large number of photographic transparencies illustrating the strata of the Earth's crust and the fossil remains by which these strata are identified and classified; also some magnificent views illustrating geological action and phenomena." Later, "fine views were shown of life on the diggings .... auriferous drifts".

Campbell continued to use the medium throughout his life, and his last known publication (1923) reproduced a number of his own photographs. However, he paid tribute for "most of the photographic work connected with the half-tone blocks illustrating this booklet" being "executed in the studio of Herbert Small Pty. Ltd.", praising their printing of amateurs' pictures and "especially for lantern slide work, in which I consider they excel".



GOLD & HOW TO GET IT,
— OR —
One Solution of the "Unemployed" Problem,
Being a POPULAR GEOLOGICAL LECTURE,
delivered in the GREAT HALL OF THE SCHOOL
OF ARTS, SYDNEY, NEW SOUTH WALES,
On MONDAY EVG., DEC. 3rd, 1894
— BY —
The REV. JOSEPH CAMPBELL, M.A., F.G.S., F.C.S.
PRINCIPAL OF S. NICOLAS' COLLEGE, RANDWICK;
niversity Extension Lecturer in Geology and Chemistry, and
Author of "Simple Tests for Minerals; or, every
Man his own Analyst

PRICE: SIXPENCE.

Prospecting for Gold on the Lachlan Tributaries

"A Good Show! Here, Lads, is Work for Hundreds"

SYDNEY.
RINTED & PUBLISHED BY WALTER BATTY, STEAM PRINTER
93 KING STREET, NEWTOWN, and at COOGEE BAY

MDCCCXCIV

Fig. 3. Title page *Gold and how to get it.*

COLONIAL AND INDIAN EXHIBITION, LONDON, 1886

Campbell joined the Royal Society of New South Wales in 1879 and, as noted above, his scientific skills were apparently acknowledged early. He was appointed a Commissioner for New South Wales to the Colonial and Indian Exhibition in London in 1886 (Colonial and Indian Exhibition 1886, 4). There is little published information on Campbell's involvement in the Exhibition.

He was gazetted (appointed) as a commissioner only on 4 March 1886, one of the last eight commissioners nominated, along with, among others, Reverend George Brown (1835-1917), missionary and scientist, and Philip Billingsley Walker, Esq., JP, Major of the Torpedo Corps and chief electrician and engineer-in-chief for electric telegraphs in Sydney. They joined the hundred or so other commissioners who had been progressively gazetted from 16 January 1885. Although preparations for the Exhibition were discussed in the Sydney press (e.g. *Sydney Mail* 16/1/1886, 6/2/1886, 13/3/1886; *Sydney Morning Herald* 18/3/1886), Campbell's departure, shortly after appointment, does not seem to have been noted, but it must have been hasty, if he was to arrive for the grand opening on 4 May.

Despite his wide interest in many matters – photography, minerals, agriculture, education – Campbell does not appear as an exhibitor in the New South Wales catalogue, but he may have supplied some of the material which was listed simply under "Commissioners".

It has not been possible, so far, to ascertain whether a local scandal had anything to do with Campbell's departure. The *Sydney Mail* (10/4/1886) notes that, after fiddling the books', an absconding Manager of the Sydney office of the Bank of New Zealand, Edward Brown Holt, had been arrested on board a ship in Brisbane, having "adopted the garb of a Roman Catholic clergyman" (Rev. Fr. Rea), and an Anglican (Rev. Mr. Paynton) for part of his escape route via Newcastle, Glen Innes and Maryborough. If Campbell's wife was closely related to this Holt, it may have seemed appropriate for the Campbells to be out of the country to avoid embarrassment.

While in England Campbell and his family lived, for a time at least, in Catford, south-east London, but he used the opportunity to travel widely and meet many people in both the technical field and in the Church. It was at this time that he joined British scientific and technical societies. The Campbells spent almost three years in England, where Joseph was apparently offered technical work, but he elected to return to Australia in 1889 to "take up his clerical and scientific work", including maintaining his own laboratory, working "sometimes in conjunction with Dr. Helms, Ph.D., Demonstrator in Chemistry at Sydney University" [probably the analyst Alfred Helms (Branagan & Holland 1985, 240)]. During his stay in England Campbell held a lectureship (he claimed), but is not specific about it. Professor K.J. Cable (pers. comm.) states that he was employed by the Society for the Propagation of the Gospel, and was for a time at Long Wittenham, near Oxford. Campbell also preached in "400 centres, including the Cathedrals of Lincoln, Ely and St Asaph".

CAMPBELL, THE GEOLOGIST

Not long before he left for England Campbell wrote one of the most successful geological books ever published in Australia. This was his *Simple Tests for Minerals, or Everyman his Own Analyst*, which ran to four editions between 1885 and 1898, the fourth being reprinted in 1900, 1913, 1925, 1931 and 1936. The first edition was a modest 77 pages and the second 90. However the third was considerably increased to 140 pages, thanks to the addition of Part II "containing a chapter on rocks .... and the appendix, the popular system of classification of rocks". The final edition and its reprints reached 180 pages.

The book owed its success to a number of factors. As Campbell noted in the introduction (to the fourth edition, 1900), it was "designed for the use of those who have not had the advantage of systematic instruction in mineralogy, and it is therefore as free as possible from technical expressions". The writing is, in fact, very clear, and the practical instructions would have made it valuable for prospectors. The book provided essential reading and use for those attracted by the mining boom of the 1880s, following the discovery of Broken Hill, and was even more called upon during the depression years of the mid 1890s and in similar downturns in the economy in later years. Campbell was concerned to be "applying science to the development of our vast mineral resources" and, because he felt it was a "cause that lacks assistance", he was "constrained to labour for it".

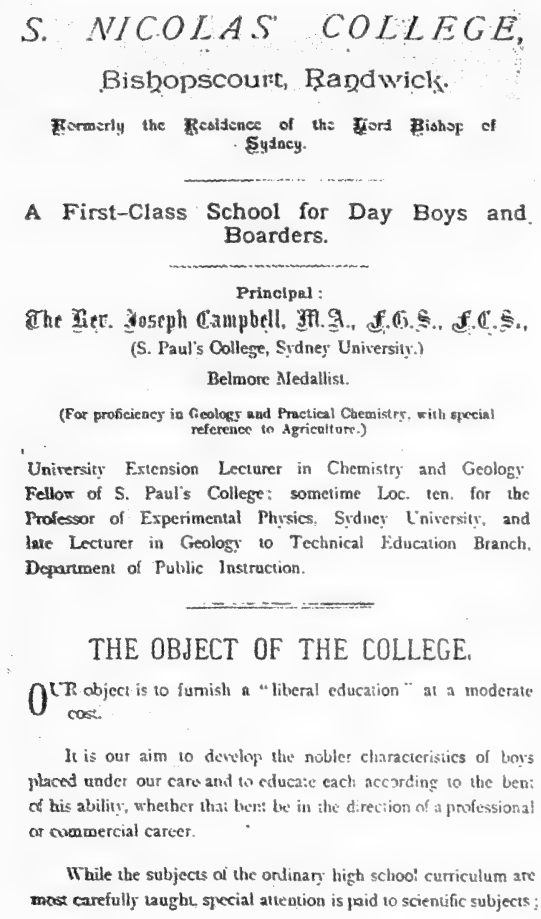
From the time of the first edition, Campbell made available his "Campbell's Prospector's Box, a very neat and portable case, 13 inches long by 6 inches wide by 6 inches deep, containing everything that is required [which] has been made in England to the order of the author for 50s[hillings]". These could be "obtained on application to the publishers of this book, Messrs. Angus and Robertson, 89 Castlereagh St, Sydney" (Fig. 4).

In 1894, during a severe depression, when many men were leaving the city and becoming prospectors, Campbell published *Gold & How to Get it: or, One Solution of the Unemployment Problem*, a 32-page pamphlet, which appeared in a second edition the following year, reduced to 27 pages, but still with illustrations from Campbell's own photographs. This booklet contained a considerable amount of local geological information, given as a popular lecture, to a large and enthusiastic audience in Sydney, and supplemented the information in his larger *Simple Tests*.

By the mid-1890s Campbell was well-established as knowledgeable in geology. Earlier he travelled around the Southern Highlands of New South Wales lecturing as a representative of the Board of Technical Education on "The Chemistry of Goldfields" (Braidwood, 12 Nov. 1890) and "The Earth's Surface" (Bowral, 8 Nov. 1890), and proposed returning for further lectures on "Precious Stones" and to visit the diamond fields in the Goulburn area. (The possible diamond field was but an isolated occurrence found in gravel at Tarlo, 16 km north of Goulburn, about 1892. The geology was reported on by J.A. Watt in 1897). The itinerant lectureships, covering agriculture, chemistry, physics, geology and mineralogy & mining, had been established by Sydney Technical College in 1883 (*Sydney Mail*, 6/2/1886). Campbell added further similar activities in 1893, when the Senate of Sydney University appointed him an extension lecturer in geology and chemistry.

Fig. 4. Campbell's Prospector's Box

According to an interview in 1897 (*Australian Mining Standard*, 15/7/1897), Campbell founded St Nicolas' School in Randwick in 1893 "for the proper training of mining experts" (Fig. 5), feeling that young gentlemen were required for the mining profession "which he has always desired to assist and elevate to a more digni-



S. NICOLAS' COLLEGE,
Bishopscourt, Randwick.

Formerly the Residence of the Lord Bishop of Sydney.

A First-Class School for Day Boys and Boarders.

Principal:
The Rev. Joseph Campbell, M.A., F.G.S., F.C.S.,
(S. Paul's College, Sydney University.)
Belmore Medallist.
(For proficiency in Geology and Practical Chemistry, with special reference to Agriculture.)

University Extension Lecturer in Chemistry and Geology Fellow of S. Paul's College; sometime Loc. ten. for the Professor of Experimental Physics, Sydney University, and late Lecturer in Geology to Technical Education Branch, Department of Public Instruction.

THE OBJECT OF THE COLLEGE.

OUR object is to furnish a "liberal education" at a moderate cost.

It is our aim to develop the nobler characteristics of boys placed under our care and to educate each according to the bent of his ability, whether that bent be in the direction of a professional or commercial career.

While the subjects of the ordinary high school curriculum are most carefully taught, special attention is paid to scientific subjects;

Fig. 5. Advertisement for St. Nicolas College.

fied position". The site of the college was apparently a fine one, and, as one would expect from a person of Campbell's energy, had good facilities for outside activities, such as cricket and tennis. If parents gave permission, students could undertake "sea-bathing" at Coogee. Advertisements in the mid-1890s for St Nicolas' College included the statement that "Photography, which is highly advantageous in reporting on mining properties, if not absolutely essential, will be practically taught".

While directing the college, Campbell continued other geological activities, and particularly some consulting. He reported on the Hanging Rock Gold Mine (October 11 1894), following a visit to Nundle (October 2-7) "at the invitation of R.H. Leiren [sic], Esq., M.L.A." (R.H. Levien [1845-1938]), who was concerned to have the Peel River Land and Mineral Company's estate at Nundle resumed and subdivided (Forbes 1986). Campbell noted the slaty country rock and, the mine occurring in diorite, commented "it is a recognized fact that diorites are intimately associated with the occurrence of gold in reefs". He described the reefs exposed in a tunnel about 150 ft long, commented that the "reefs are only scratched so far", and, believing that they would extend to a considerable depth, recommended a 1000 ft level tunnel which he expected would "expose richer stone" at a probable cost of £1500 to £2000. Campbell's one-page report, accompanied by another, earlier, report by M. Birrell, M.E. and a plan (author unidentified) appeared in the prospectus of the Tamworth Gold Mining Co. Limited for a proposed issue of £55 000 @ £1 to boost the company's capital. Although a London company, it boasted an advisory local committee of Sir Henry Parkes and several gentlemen of Tamworth. Campbell, as curate at Surry Hills in the early 1880s, had some contact with Parkes through Parkes's sister who was living in the parish.

Campbell's restless nature precluded him from achieving much similarity to the clerical geologists Clarke and Tenison Woods. His grasp of geological principles was sound, but he was not concerned to develop this side of his knowledge. His work took him into the applications of geology, the identification of minerals and their treatment and, unlike the other two, Campbell devoted considerable time to teaching, both in formal and informal situations. As he urged on more than one occasion "look not coldly on science, but call her to your aid" (Campbell 1894).

TREATMENT OF REFRACTORY ORES – THE "THERMO-HYPERPHORIC" PROCESS.

Campbell's interest in ore treatment seems to have begun while he was at Glen Innes in the 1880s and probably intensified during his visit to Britain between 1886 and 1889. He directed particular attention to the extraction of gold. In his *"Gold & How to Get it"* (1894) lecture, Campbell went into some detail about a process which he called "Thermo-Hyperphoric", using heat and removing refractory substances, and he discussed the costs involved in producing the metal.

The method consisted of passing steam over red-hot coke producing water-gas (hydrogen and carbon monoxide), which was passed into closed furnaces, into which was fed crushed ore. The furnaces were heated to between 1200° and 1800°F (i.e. 650 to 1000°C) and, after treatment from two to four hours, "depending on the complexity of the ores, all impurities which interfere with the amalgamation of the gold are removed, or are so modified by the chemical action of the gases, that the precious metal is left quite pure". We can gain some idea of the method from the two photos reproduced in Campbell's 1894 publication, which he labelled "The view of the furnace erected at the Sir Walter Scott Mine at Cangai, Clarence River District for carrying out the hyperphoric treatment" and "A view of the pans used for grinding and amalgamating the ore after it is treated" with their explanatory captions (Figs 6 & 7). He noted it was the "invention of Messrs. Lockwood and Chappel [sic]" and, with the "assistance of one of the patentees [Lockwood] I erected this plant and spent four months in the erection of the Works and the application of the treatment–working often day and night to give it a fair trial" (Campbell 1894).

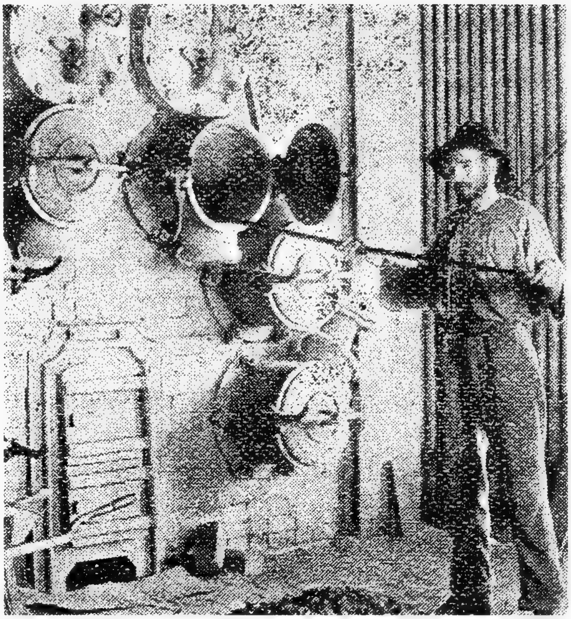


Fig. 6. Furnace for the "Hyperphoric treatment", Cangai Mine.

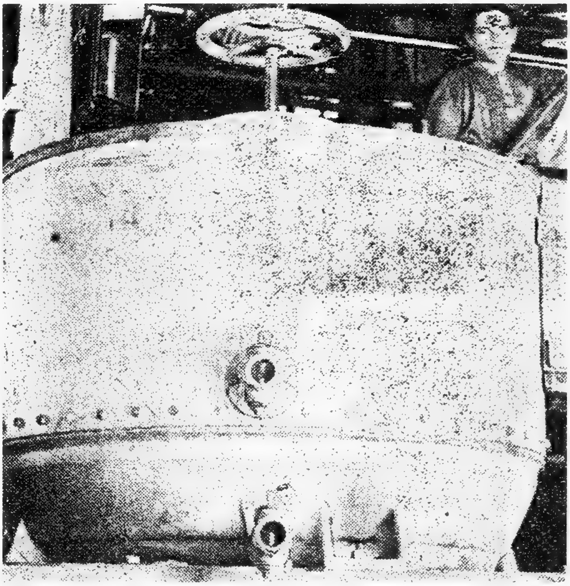


Fig. 7. Grinding pans for ore treatment, Cangai Mine.

In the several years before his premature death in 1892, the Government Geologist, C.S. Wilkinson, was also considerably interested and involved in the treatment of ores. In this matter he was briefly associated with Campbell, not long returned from overseas. The first notice of this co-operation is in Wilkinson's diary for 24 July 1889: "Rev. Mr. Campbell called and presented me with a share in patent process for treating auriferous and argentiferous ores by steam converted into hydrogen and carbonic oxide gases—on the same principle as the process my father [David Wilkinson] patented in 1857—on this account he requested my acceptance of the share". Five days later they went together to "Mr. Chapple's [sic] place at Newtown", where he showed them his superheated steam model furnace "at work for treating pyritous stone", which produced some moss gold. Wilkinson's diary of 18 Sept 1889 contains a cutting from the Melbourne newspaper *Argus,* written apparently some years earlier (6/10/1886?) by his former colleague Cosmo Newbery (on the Victorian Geological Survey in the 1860s). Wilkinson had kept in touch with Newbery, who was then working in the National Museum of Victoria, and met him in February 1889 in Melbourne, during the AAAS meeting there. The cutting was a letter concerning methods of gold treatment by a Mr. Edwards and suggests Wilkinson's continuing fascination with the problems. Wilkinson also recorded (18 Dec. Wed [1889]) "in morning with Pittman inspected Chappell [the correct name] and Lockwoods process at Birkenhead", but there is no mention of Campbell being present.

Wilkinson's quite extensive experimentation and patenting of a fuel injection process was done in association with Messrs Plummer, Rock and others, the work being carried out at Morrison's works at Strathfield, but Campbell does not seem to have been involved. However, Campbell certainly continued his laboratory work to improve his gold ore treatment, using water-gas during his time at St Nicolas. Between October 1896 and March 1897 he visited America and England, lecturing *inter alia* at Berkeley and discussing his method with technical experts and demonstrating it, apparently with some success. Royal Mint officials in London approved and an international syndicate was set up to make it available world-wide, while Campbell gained support to form a company to work and treat the Montezuma ores at Te Aroha in the Coromandel district of New Zealand, the proviso being that Campbell himself should act as managing director, which he agreed to do, resigning his "important work in N.S.W .... to devote twelve months to that work, which he feels will enable him to be of greater service to his fellow men".

On 17 July 1897, Campbell left St Nicolas, travelling to New Zealand on the *Westralia*, to begin work on the ores of the Hauraki Peninsula. That year he published several articles on "The Goldfields of the Hauraki Peninsula" in the *Transactions of the Federated Institute of Mining Engineers*, having been elected an associate member in December 1896, where he was named as "Consulting Geologist, St. Nicholas [sic] College, Randwick". Campbell's work at Hauraki was criticised by the experienced Scottish geologist Henry Cadell (1860-1934) in his own paper on the region (Cadell 1896). The Hauraki field had been the topic of a long paper by F.W. Hutton, given at the first AAAS meeting in Sydney in 1888, which Campbell apparently attended. Campbell's interests by 1897 were of course directed more particularly to the treatment of the very refractory ore, rather than to the geological aspects of the ore-body. The treatment works included furnaces heated by gas and chemical treatment by water gas at a temperature of 2000°F. Erected at a cost of £8000, the installation included a laboratory.

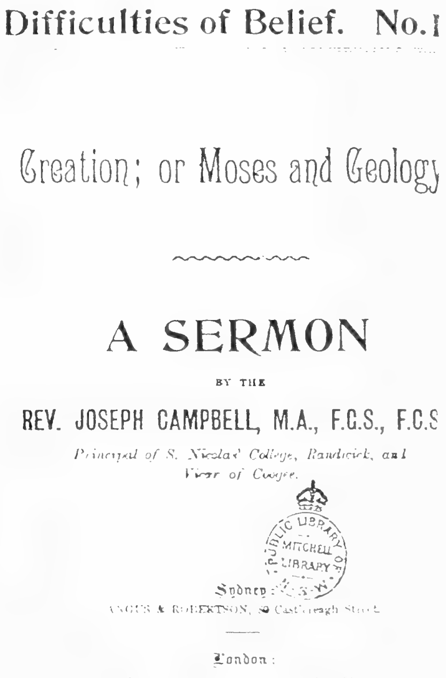
Campbell remained at Hauraki until 1901, but it is not clear how successful the project was. The author has not discovered the reason for his move to Christchurch in the South Island in 1900, but there seems to have been a temporary cessation of scientific and technical work and a return to full-time church work, which may have been the result of the death of his wife in England that year.

CAMPBELL, THE PREACHER

From all reports, Campbell was a fine preacher, attracting congregations in the hundreds. His sermons were always delivered extempore from brief notes. Those which were published were usually on request and written after delivery. Somewhat surprisingly, he noted that one sermon "occupied 40 minutes of delivery, and, as now presented, is necessarily curtailed". The *New Zealand Illustrated Magazine* (August 1900) noted that Campbell's "intimate knowledge of geology assisted him materially, doubtless, in the preparation of a course of sermons which he published illustrating in a very practical manner the intimate relations between religion and science, thus explaining incontestably seeming incongruities and biblical difficulties by the aid of science .... To his varied experiences and intimate knowledge of life in all its phases, together with his evident belief that an occasional dash of humour is by no means out of place in the pulpit, he owes his great popularity and usefulness as a preacher".

The first of Campbell's sermons was published in 1884 (by a publisher, Loxton, not associated with his earlier general publications). Although titled *"Confirmation Series 1 No. 1"* it was the only one of this proposed series. However, it may have been changes of circumstance that prevented the publication of other pamphlets, for Campbell must have been busy preparing his first edition of *Simple Tests* ...., published the following year. A little later he was off to England for the Indian and Colonial Exhibition.

Not till 1895 did publications on religious themes resume, with *"Difficulties of Belief, No. 1"*. This covered the topic *Creation; or Moses and Geology* (Fig. 8), a subject that had long interested Australian Anglican clergy such as C.P.N. Wilton and J.D. Lang. For this twenty-page publication Campbell stayed with the publishers Angus & Robertson, who were already making money from his mineralogical text. Perhaps the pamphlet attracted some attention, for *"Difficulties of Belief, No. 2"* ap-



Difficulties of Belief. No.1

Creation; or Moses and Geology

A SERMON

BY THE

REV. JOSEPH CAMPBELL, M.A., F.G.S., F.C.S

Principal of S. Nicolas' College, Randwick, and
Vicar of Coogee.

Sydney:
ANGUS & ROBERTSON, 89 Castlereagh Street

London:
Y. J. PENTLAND, 38 West Smithfield

Fig. 8. Title page of *"Difficulties of Belief, No.1."*

peared the same year, with an associated theme in the sub-title *"Evolution and the Antiquity of Man - A Sermon"*. However Phillips (1981) notes that interest in the Science — Religion relationship had waned somewhat in the 1890s from the 1880s.

Campbell's final religious publication was produced in 1902 during the heyday of Spiritualism. *"In the Spirit World"*, a 45-page 8vo effort was published in Christchurch, New Zealand. This pamphlet was in fact three sermons: "Some Character[istic]s of the Spirit World", "Our Dear Ones in the Spirit World" and "Seeing Angels in the Way", delivered at St Paul's Church, Papanui, on Easter Day, 30 March 1902, and two Sundays during April 1902. The sermons were recorded in shorthand by the church organist, Miss Alice Searell, and Campbell apparently made few changes. Campbell affirmed that the spirit-world is co-extensive with the physical world and that we are in it all the time. These sermons would have been given not so long after his (first) wife died in England, and when he may have been only recently reunited with his two daughters, whom he reported much later as living in New Zealand.

Campbell was not averse to criticizing the Church. In his published lecture on gold (1894), when speaking of the need for a properly organized system of work, he recommended unionistic principles "purified by the elimination of that detestable selfishness which ruins everything both in Church and State. Church and State I say. The whole system of both needs renewing. Both are more or less corrupt, and, as I have just hinted, through selfishness".

Campbell's move to North Queensland in 1903 marked the end of his sporadic forays into religious writing, and he seems to have changed direction towards agricultural pursuits. He was possibly beginning to be a little eccentric, as he was later aware that many people regarded him as such. However, he was extremely popular in Cairns during his period as Archdeacon.

Campbell's comments in 1922 on his religious pursuits might be regarded by some as somewhat patronizing. He noted, at this time, that he took Holy Orders "not as a living, but to bring Science to bear on Theology, and to help the Church in my leisure". He continued "I have held four Cures for periods of three to five years: but beyond that, my Church work has been honorary. However, the majority of Church Dignitaries in the North do not approve of my broad teaching. It matters not, for Science rules the roost, and henceforth my lectures will be on the broad principles of the early Christian Church, the keynote being The Service of Man' ". However, it seems that the Bishop of North Queensland objected to Campbell because of his commercial activities rather than his 'broad' beliefs.

THE KAMMA LABORATORY—STUDIES OF TROPICAL RESOURCES, 1910-22 AND THE NORTH QUEENSLAND INTELLIGENCE BUREAU

The Service of Man was certainly epitomized by Campbell from the time of his arrival in Cairns for a period of nearly twenty years. When he moved to North Queensland in November 1903, Campbell retained his interests in mining and geology, holding a weekly class in practical mineralogy for St John's Men's Club. The quality of Campbell's teaching can be estimated from one of these lectures, published in the local press. It is a beautiful and clear exposition of the nature of crystals and crystallisation. In 1905 he gave a lecture tour on mining and he continued his geo-

Fig. 9. Campbell and one of his daughters displaying a *Caravonica* cotton tree.

logical interests at least until 1909. In 1905 there appeared Campbell's last specifically geological booklet, *"The Key of Knowledge for Miners or What's the Value of this Ore?"*, together with "The Miner's Assaying Cabinet" "containing everything required for applying the methods described and .... testing the value of any ore he might happen to come across". At this time he lived in 'The Bungalow', which is now commemorated by the inner Cairns suburb of the same name.

However, there were other scientific and technical problems in the region which turned Campbell's attention to his other early interest, agriculture, believing that he could make a contribution to the development of this part of the continent. It seems clear that he did so with a vengeance, as is shown by Jones (1976) and by the files of the *Cairns Post*. He saw cotton as a potentially valuable crop (Fig. 9). He apparently experimented with different varieties, but came to the conclusion that a long-stapled variety known as *Caravonica* (named by an Italian, Dr. Thomatis, who encouraged this crop in the Cairns district) was most suitable. Campbell believed it was related to "the original sea island variety known as *Gossypium Barbadeuse*" and had "established itself in Northern Queensland", probably in the 1870s. Campbell worked on this strain in association with a German company that took over from Dr. Thomatis and exhibited a bale at the great Franco-British Exhibition in 1908, when it was awarded a Diploma of Honour and was classed as one of the world's best long-stapled cottons.

After resigning his clerical position in September 1909, Campbell went to Germany and England for a year or more. He was instrumental in forming a company in London to grow cotton on a large scale and entered into contracts with Germany to supply it at one shilling per pound. He wrote: "It has always been worth 6d. per lb. more than American middlings. Seed was subsequently obtained from me by the late Director of Agriculture in Java (Dr. Van Breda de Hann), and it has been grown in Flores for the Dutch to the exclusion of all other varieties. But I had no Government support beyond a 10 per cent bounty and cheap aboriginal labour: and when the bounty ceased in 1915 and the cost of aboriginal labour was increased threefold, and the war nullified my contracts, I was compelled to turn my cotton fields into cane fields and give easy terms to settlers, most of whom are now prosperous cane farmers. Two are now driving their motor cars, and I tell the others that I see their cars just below the surface of the ground, and that soon they too will be driving them" (Campbell 1923).

While not recommending cotton as a producer of large dividends for companies producing directly, Campbell recommended cotton growing for "suitable men on suitable land" and went on to detail costs and yields in a very thorough practical way. He also commented briefly on the possibility of reopening trade in cotton with Germany. Jones (1976) and Lloyd (1983) discuss other problems that Campbell had in relation to his cotton ventures, such as the destruction of his ginnery by fire in 1912 (see also *Cairns Post* 16/9/1912).

At the end of his little general treatise on tropical agriculture (Fig. 10), Campbell (1922) noted "if sufficient interest is taken, we propose to publish as soon as possible, at 2/6 [price], *A PRACTICAL TREATISE ON COTTON-GROWING IN AUSTRALIA* (The industry which will help to ensure the future and progress of the Empire) by Demonstrator JOSEPH CAMPBELL M.A., M.I.M.E., The Cotton Expert and Advocate of the far North, entitled 'King Cotton, The Cloth of the World' ". This work does not appear to have been printed.

Jones (1976) reports on the extraordinary range of Campbell's agricultural experiments: "He made textile fibres from *Sida retusa*, jute, Chinese burr; made a very superior paper from blady grass and a more common commercial paper from pandanus. He produced native dyes at Gossypium Park achieving a true indigo, navy, royal, black, khaki, gray, brown, pink, green and yellow. Other products were dispeptic papain from pawpaw, varnish from native gum, and he extracted candle nut and cotton seed oil".

Jones (*op. cit.*) also records Campbell's contribution to the welfare of Cairns during the Australia-wide influenza epidemic of 1919, and at the time of a major shipping strike in the same year, which effectively isolated the town. The Queensland Government backed down from a proposal to ship flour from Sydney and Melbourne and "Cairns was almost brought to her knees .... it was Joseph Campbell, the agricultural scientist who managed to keep the town going, if on short rations, by converting his pulp paper machine to crush a maize flour. He was putting through two tons of maize flour a day, so long as the maize lasted".

"COMMENTS AND A PLAIN STATEMENT OF FACTS LEADING UP TO A DEFINITE OFFER OF HELP"—THE 1923 PAN-PACIFIC CONGRESS

In 1888 Campbell was registered as attending the first meeting of the Australasian Association for the Advancement of Science, held in Sydney, he being then resident in Glen Innes, but he does not appear to have participated in any of the later AAAS meetings. He withdrew from most scientific societies about 1900.

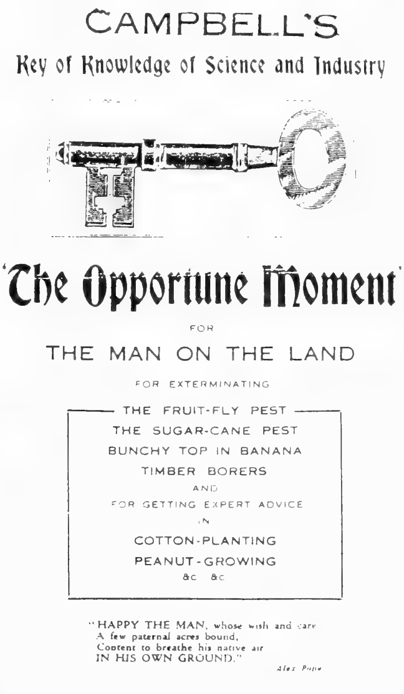
Although Campbell is not listed as a member or corresponding member of the Second Pan-Pacific Congress, the second part of which was held in Sydney in August 1923, he attended at least the opening meeting. He recorded at the beginning of his pamphlet "*Campbell's Key of Knowledge of Science and Industry*" (Fig. 11) under the above heading ("Comments..".), with perhaps a touch of sadness, "although one of Australia's oldest workers in Science and Industry, spending and being spent in the noble cause for over 35 years, I was not invited to be a member of the Congress, and was thus denied the privilege of giving to the world an outline of the results of my investigations per the medium of the published transactions .... we cannot all be leaders — some must be non-coms .... In the yearly increasing army of modern scientists there are many as well qualified to lead in the application of science to industry as the chosen delegates to the Science Congress".


North Queensland • Intelligence Bureau
ARCADIA, MULGRAVE ROAD SOUTH CAIRNS, N.Q.
The Rendezvous of
DIRECTOR OF THE BUREAU
THE INTELLIGENCE BUREAU
SCIENCE. INDUSTRY. CHRISTIANITY.
Ego sustineo tres personas [Cicero]
(I appear before you in a threefold attitude)
Sunday Afternoon

Fig. 10. North Queensland Intelligence Bureau.

Campbell went on to confirm the need for specialization, and to praise the local press "on the admirable epitome given of the addresses and proceedings". "We who have left the field of pure science of our 'Varsity days to labour in the broad field of applied science, amid scenes strange and new, are glad to have the results of our fellow-students who are in the happy position of having their well-equipped laboratories and their costs defrayed by their various governments". He continued to discuss policies for encouraging the use of science in various activities, and particularly his then major interests, cotton, soft timber and insect pests. He invited readers to attend one of his lectures, discussed a considerable number of plant problems in detail, and considered some of the social and political implications. Finally he noted "I have left these bright scenes [illustrated] in the far north to come to New South Wales and tell how this can be done. Now is the **Opportune Moment** for the Man on the Land". The cover of this, his final pamphlet states "You may interview Demonstrator Campbell at the Science and Industry Intelligence Bureau, 155 Phillip Street, Sydney, generally between 10 and 1 daily, but preferably, by appointment, as he is a busy man" (Fig. 11).

And so he certainly remained until his death. Campbell probably fell on hard times with this offer, which was likely to be ignored by the worthy burghers of Sydney. Whether his family was still with him is


CAMPBELL'S
Key of Knowledge of Science and Industry

"The Opportune Moment"
FOR
THE MAN ON THE LAND
FOR EXTERMINATING
THE FRUIT-FLY PEST
THE SUGAR-CANE PEST
BUNCHY TOP IN BANANA
TIMBER BORERS
AND
FOR GETTING EXPERT ADVICE
IN
COTTON-PLANTING
PEANUT-GROWING
&c &c

"HAPPY THE MAN, whose wish and care
A few paternal acres bound,
Content to breathe his native air
IN HIS OWN GROUND."
Alex Pope

Fig. 11. *"Campbell's Key of Knowledge of Science and Industry"*.

uncertain. However, another former St Paul's College man came to his aid in 1926. This was Right Reverend L.B. Radford, a former warden of the college, a scholar, and at that time Bishop of Goulburn. Radford offered Campbell *locum* positions in the diocese, in Wagga, Bodalla, and in other rural parishes. It was at Barmedman in the Wagga Diocese that Campbell died on 17 October 1933.

Thus one of Australia's most remarkable applied scientists fades from our sight. Did he influence many people during his active and interesting life? I believe so.

COMMENT

Campbell's period as Acting Professor at the University of Sydney in 1882-3 and as Extension Lecturer is not recorded in the University's official history (Turney *et al.* 1991), nor does it receive mention in the book on Professor John Smith (Macleod 1988); the *Australian Dictionary of Biography* office has no record of Campbell's life. His work for the Department of Technical Education as itinerant lecturer throughout New South Wales is forgotten, as is his pioneer work in photography and ore refining, but his experiments in tropical agriculture are at least remembered where they were carried out and some of his experimental equipment is in the Queensland Museum. His sermons, which undoubtedly stirred many thousands, have also been consigned to dusty back shelves of theological libraries. How can we do this to a brilliant man, a man of culture and deep learning, yet a man who was not afraid to dirty his hands for the people and country he clearly loved and laboured for during almost seventy years? How many forgotten Campbell's are there in Australia's history?

ACKNOWLEDGEMENTS

The basis of this manuscript comes from Campbell's own publications, which are listed below. While there is occasional inconsistency concerning dates, evidence from other sources shows that Campbell's data about his life and work are generally very reliable.

The author came across Campbell by accident, when searching through the *Australian Mining Standard* some years ago, and then found a copy of his *Simple Tests,* which contained a little more information on his life. He then turned up briefly in C.S. Wilkinson's diaries of 1889-90, which the author was privileged to see through the courtesy of a descendent, Mrs. Elizabeth Wilkinson of Castle Cove, Sydney. When transferring the late Tom Vallance's card index of Australian geoscientists and miners to a database it was a pleasure to find that Tom had done a little more searching, tracing Campbell's clerical activities to Cairns.

Particular thanks are due to Ms Kass Gardiner, Special Services Librarian, Cairns City Council, who made the author aware of the historical work of Dorothy Jones, provided portions of her published book and numerous references to Campbell in the *Cairns Post*. Pat Broughton of the Cairns District Historical Society also followed up the author's requests for further information and provided illustrations and Campbell's most illuminating lecture on crystallography.

Because of Campbell's habit of placing copies of his publications in the New South Wales Public Library (under its various names), the story has gradually unfolded and the author is grateful for assistance from numerous librarians in the Mitchell Library, the Library of New South Wales and Fisher Library of the University of

Sydney (particularly the Rare Books Department). Thanks go to Professor K.J. Cable for filling in the details of Campbell's last years and death and other aspects of his clerical life.

Finally the author has to thank Professor David Oldroyd for his very helpful review of the completed manuscript and his recommendations for amendments, which have greatly improved the text of the paper.

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Thesis Abstract

SOME CARDIOVASCULAR MORPHOLOGICAL SPECIALISATIONS AND ASPECTS OF CARDIOVASCULAR CONTROL IN THE LOWER VERTEBRATES, *CARCHARHINUS MELANOPTERUS, RHINOBATOS TYPUS, NEOCERATODUS FORSTERI* AND *ARIUS GRAEFFEI*

LISA K. CHOPIN

Abstract of Thesis submitted for the Degree of Doctor of Philosophy at The University of Queensland

Catecholamines released from chromaffin cells appear to play an integral role in the regulation of the cardiovascular system of lower vertebrates. Chromaffin cells are present in the axillary and suprarenal bodies of *R. typos* and *C. melanopteros*; in the atrium, intercostal arteries and the posterior cardinal vein of *N. forsteri*, and in the posterior cardinal vein in the head kidney of *A. graeffei*. Although chromaffin cells have been described in the sinus venosus of other elasmobranchs, there are no chromaffin cells here in *R. typos* and *C. melanopterus*. Chromaffin tissues in *N. forsteri* and *A. graefei* exhibit tyrosine-hydroxylase-immunoreactivity. Ultrastructural studies show that chromaffin cells contain large numbers of chromaffin-positive, electron-dense, membrane-bound granular vesicles. Two cell types (presumably adrenaline- and noradrenaline-storing cells) can be distinguished on the basis of granule electron-density in *R. typos, C. melanopteras* and in *A graeffei* but only one cell type can be distinguished in *N. forsteri*. Chromaffm cells receive an innervation in these lower vertebrates, and synaptic specializations have been observed in close association with chromaffin cells.

The role of the autonomic nervous system in the regulation of the cardiovascular system is investigated. Physiological and anatomical studies failed to reveal evidence for an autonomic innervation of the branchial vasculature of *C. melanopterus*. Perfused gill preparations are responsive to noradrenaline with vasoconstriction at high concentrations and vasodilatation at low concentrations. The branchial vasculature constricts via muscarinic receptors in response to acetylcholine. The distribution of the caudal autonomic nervous system of *C. melanopteras* and *R. emus* is similar to that of other elasmobranchs.

Adrenergic nerve fibres were demonstrated histochemically. Isolated tail preparations in *R. typos* and *C. melanopterus* are responsive to perfused catecholamines and acetylcholine which both vasoconstrict the tail vasculature. Nerve stimulation experiments gave inconclusive results in these preparations. The functional role of the autonomic nervous system in regulating the tail vasculature of elasmobranchs remains controversiaL This is the first study to demonstrate catecholaminergic nerves in the dipnoans. The pulmonary artery and

branchial vasculature contain catecholamine fluorescent nerves which have the ultrastructural features of catecholaminergic nerves. Adrenergic nerves, revealed immunohistochemically, are associated with the systemic secondary vessel system of the teleost, *A. graeffiei.* Vascular casts are used to describe the systemic secondary vessel system in *A. graeffei*, and some fine structural features of this system are described for the first time in this study. No morphological features of such a system are present in *R. typus, C. melanopterus* or *N. forsteri*. The measurement of a low erythrocyte content in the cutaneous veins of *R. typus* suggests that a fictional shunting of elythrocytes could be occurring.

The four species studied share many cardiac ultrastuctural features. Exposure of *R. typus* to a low salinity environment for three days resulted in some morphological and morphometric changes in myoendocrine cell ultrastructure presumably due to an increase in atrial natriuretic or related peptide production.

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Thesis Abstract

"A GREAT DEAL OF SICKNESS"
Introduced Diseases among the Aboriginal People of Colonial Southeast Australia 1788-1900

PETER J. DOWLING

Abstract of a Thesis Submitted for the Degree of Doctor of Philosophy,
The Australian National University, Canberra

Palaeopathological studies have sought to build up a picture of Australian Aboriginal health before European settlement in 1788, and epidemiological studies of Aboriginal health in the twentieth century are now legion. But, despite a growing body of literature on Aboriginal history in the intervening colonial period, this remains an under-studied period from the viewpoint specifically of Aboriginal health. This thesis is a contribution to filling that gap through an examination of documentary and skeletal evidence on the changing biomedical situation experienced by Aboriginal populations of Southeast Australia from 1788 to 1900.

This thesis examines one of the major biological components of this change - the diseases that were introduced into Australian Aboriginal populations during the process of colonisation. The epidemiology, timing, diffusion of diseases are considered with specific attention given to infectious and respiratory diseases that were responsible for causing major epidemics of morbidity and mortality.

A medical model for the contact period in the late 18th and 19th centuries is proposed. This model considers three major stages in the disease environment of Aboriginal populations in Southeast Australia; a pre-contact stage with endemic pathogens causing chronic diseases and limited epidemics, an early contact stage where introduced exotic human diseases cause severe epidemics of infectious and respiratory diseases among Aboriginal populations, and a third stage where remaining Aboriginal populations were institutionalized on government and mission settlements and were subjected to a high level of mortality from the introduced diseases.

The major epidemic diseases during the early contact stage were smallpox, syphilis, tuberculosis, influenza, and measles. Each of these diseases was responsible for excessive morbidity and mortality. During the period of institutionalisation infectious and respiratory diseases were responsible for over 50% of recorded deaths on 8 separate Aboriginal settlements in Southeast Australia. The major diseases recorded as causes of death were tuberculosis, bronchitis, pneumonia, diarrhoea and dysentery.

Aboriginal and non-Aboriginal Australian infant mortality rates are calculated to provide an indicator to compare the state of health of the two populations. Aboriginal rates were high when compared to the non-Aboriginal populations of Victoria and South Australia. The rates reveal a substantial health differential between Aboriginal and non-Aboriginal populations. Aboriginal infant mortality has improved into the latter quarter of the twentieth century but the corresponding improvement in non-Aboriginal infant mortality has been at a much higher rate. The gap between the health status of each has widened rather than narrowed over the last one hundred years.

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Thesis Abstract

INTEGER FACTORISATION ALGORITHMS

KEVIN JOHN FERGUSSON

A Thesis submitted for the Degree of Master of Science University of Western Australia.

This thesis concerns itself with the problem of decornposing an integer into its prime factors. The problem can be equivalently posed as the question: Given the number n, what whole numbers a and b (both larger than one) will multiply together to give n? This problem has received much research interest because its difficulty of solution is exploited in many cryptosystems, in particular, the popular RSA cryptosystem discovered by Rivest, Shamir and Adleman at MIT in 1977. A survey of integer factorisation algorithms is presented as well as some of my attempts at generalizations or variations of existing methods in the hope that this comprises a comprehensive overview of the current state of the art of integer factorisation.

The first chapter of this thesis introduces the problem of integer factorisation and provides detailed analyses of algorithms such as Pollard's rho method and Brent's method. Chapter one also provides an alternative analysis of an algorithm which is simpler than Pollard's rho method. Random walks in number fields are suggested as an alternative to the rho methods, which are basically random walks in congruence classes of the integers.

In the second chapter, a generalization of the p-1 method and the p+1 method is developed using cyclotomic polynomials and analysed. Specific cases of this algorithm then are implemented.

The theory of elliptic curves leads the reader into the elliptic curve method of factorisation in the third chapter, and this theory provides the basis for a running time analysis of the algorithm. The fourth chapter involves the theory of binary integer quadratic forms in developing the class group method of factorisation. Various implementations of the algorithms are presented and analysed in the hope that this might lead to some more general method. Also, auxiliary algorithms for these previously mentioned methods of factorisation are presented with some generalisation attempted. One popular example of an auxiliary method is a random walk among the group elements. The other methods deviate slightly from this example.

Chapters six and seven explore methods of integer factorisation which attack the problem from a different viewpoint, notably the continued fraction method, the quadratic sieve, the multiple polynomial quadratic sieve and the number field sieve. Attempts are made to generalise these algorithms or to provide variations of them in the hope of an improvement in running time.

The thesis concludes with a summary of the theoretical running times of the algorithms.

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Thesis Abstract

MALE STERILE MUTANTS OF ARABIDOPSIS
Cloning of a T-DNA tagged gene

JULIE GLOVER

Abstract of a Thesis Submitted for the Degree of Doctor of Philosophy at
The Australian National University, Canberra

Fertile pollen is the culmination of physiological, biochemical and morphological processes requiring the coordinated spatial and temporal expression of a large number of gametophytic and sporophytic genes. Although male sterile mutants have been described in many different plant species, few of the genes responsible have been cloned. This study describes the screening of 21 T-DNA generated, reduced fertility lines of *Arabidopsis thaliana* in order to identify a tagged male sterile mutation and clone the interrupted gene. In two lines the male sterile mutation was segregating with a T-DNA insert. Further studies focused on one of these, Line 178.

The nuclear male sterile mutation in Line 178 was found to be allelic with a previously described EMS-generated mutant, *ms5*. The phenotype of this new, tagged allele (*ms5-2*) is the result of complex interplay between genetic and environmental factors. Using both alleles the *ms5* mutation was mapped to chromosome 4. Plant DNA adjacent to the T-DNA was isolated from the *ms5-2* mutant plants and isolation of the equivalent wild-type sequences is described. Two open reading frames were detected in the region of T-DNA integration; one of them corresponding to a ß-tubulin gene (*TUB9*) that has previously been sequenced. The T-DNA has integrated 601 bp downstream of the stop codon for this *TUB9* gene and transcript levels appear unaffected.

A novel gene that was interrupted by the T-DNA insertion was identified and a cDNA isolated from an Arabidopsis flower bud library. Northern analysis failed to detect expression of the putative *MS5* gene (*pMS5*) in flower buds or leaves of wild-type plants. The T-DNA has inserted into the coding region of this gene, truncating the protein by 112 amino acids. Southern analysis suggests that *pMS5* may be a member of a small gene family. The predicted protein sequence for this gene has homology with two expressed sequence tags (ESTs), one from Arabidopsis and one from rice. These homologies are limited, suggesting that these are members of the *pMS5* gene family rather than being functional homologues. Complementation experiments were initiated in Arabidopsis to determine whether this gene corresponds to the *MS5* gene.

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Thesis Abstract

DEVELOPING EFFICIENT WHITE CLOVER (*TRIFOLIUM REPELS* L.)
Breeding Strategies for the Dryland Summer Moisture Stress Environments of Australia

M. Z. Z. Jahufer
Abstract of a Thesis submitted for the Degree of Doctor of Philosophy
at The University of Queensland

Summer moisture stress has been identified as a major constraint to vegetative persistence and herbage yield of white clover in Australia. Genetic improvement of vegetative persistence and herbage yield of white clover for dryland summer moisture stress environments is a key objective in the development of new cultivars for the Australian grazing industries.

The Ph.D. research program was focused on: (i) studying the genotypic variation for stolon and other morphological attributes, including seasonal herbage yield, present in a world sourced collection of white clover germplasm accessions maintained at the Genetic Resource Centre, Glen Innes, New South Wales (NSW); (ii) examining the effects of environmental variation for level of moisture stress during summer on the expression of variation for stolon attributes and herbage yield; (iii) estimating quantitative genetic parameters for stolon morphological attributes and herbage yield; (iv) testing the hypothesis that crossing of morphologically diverse plants may be a useful strategy for breaking the negative association between vegetative persistence and herbage yield; and (v) developing an efficient breeding strategy for the improvement of vegetative persistence and herbage yield of white clover under dryland summer moisture stress conditions of Australia.

Morphological characterisation of the total world sourced collection of white clover germplasm (439 accessions) was conducted on different batches of accessions over a period of five years under dryland summer moisture stress conditions. There was significant ($P<0.05$) genotypic variation among accessions for all the morphological attributes including herbage yield. The performance of the two check cultivars, Haifa and Huia, included in each batch provided a basis for adjustment of the data for attributeby-year interaction effects by estimation of Best Linear Unbiased Predictions (BLUPs). Pattern analysis enabled identification of germplasm accessions that could be used for the development of white clover cultivars through recurrent selection. The germplasm collection was also found to be deficient in genotypes with high stolon density, high number of branches, high number of rooted nodes and large leaves.

Genetic families produced using the North Carolina I (NCI) mating design were evaluated for herbage yield and key stolon attributes conferring vegetative persistence in dryland summer moisture stress and irrigated treatments over three years. The combined analysis of variance of the families across environments and years indicated the presence of genotypic variation for all the stolon attributes and summer herbage yield. Large genotype-by-environment-by-year-interactions were estimated. The phenotypic and genotypic correlation coefficients between the attributes, estimated for the genetic families, indicated that the undesirable negative association between vegetative perenniality and herbage yield had been changed. This provided strong evidence that the negative correlation coefficients reported from other studies are a result of linkage and not pleiotropy.

The following recommendations were made to improve the efficiency of breeding white clover for dryland moisture stress environments in Australia: (i) upgrade the germplasm collection to compensate for plant types that are deficient; (ii) generation of new genotypic recombinants by crossing morphologically diverse accessions; (iii) use of multi-site testing during all stages of evaluation in the breeding program; (iv) use of progeny tests to identify parents with good general combining ability; and (v) use of row-column experimental design methodology and pattern analysis methodology at all stages of testing as statistical tools to enhance the opportunities for identification of useful germplasm from the world collection and cultivars with improved adaptation from the breeding program.

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Thesis Abstract

NGOs, PEASANTS AND THE STATE: TRANSFORMATION AND INTERVENTION IN RURAL THAILAND, 1970s-1990s

RAPIN QUINN

Abstract of Thesis Submitted for the Degree of Doctor of Philosophy
The Australian National University, 1997

This study examines people-centred Thai NGOs trying to help peasants empower themselves in order to compete better in conflicts over land, water, forest, and capital, during the 1970s to 190s. The study investigates how the NGOs contested asymmetric power relations among government officials, private entrepreneurs and ordinary people while helping raise the peoples confidence in their own power to negotiate their demands with other actors.

The thesis argues that the NGOs are able to play an interventionist role when a number of key factors coexist. First, the NGOs are able to understand loci situations which contain asymmetric power relations between different actors, in relation to current changes in the wider context of the Thai political economy and seize the time to take action. Secondly, the NGOs are able to articulate a social meaning beyond the dominating rhetoric of the 'state' and the 'capitalists' which encourages the people's, participation in collective activities. Thirdly, while dealing with one problem in social relations and negotiation with local environment, the NGOs are able to recognise new problems as they arise and rapidly identify a new political space for the actors to renegotiate their conflicting interests and demands. Fourthly, the NGOs are able to recreate new meanings, new actors and reform their organisffions and networks to deal with new situations. Finally, the NGOs are able to effectively use three pillars of their movement, namely individuals, organisations and networks to deal with everyday politics and collective protest.

The case studies in three villages in Northern Thailand reveal that the NGOs were able to play an interventionist role in specific situations through their alternate development strategies somewhat influenced by structural Marxism. The thesis recommends that the NGO interventionist role be continued so as to overcome tensions within the NGO community, for instance, between the NGOs working at the grassroots level and the NGOs working at regional and national levels (including NGO funding agencies); local everyday conflicts; and the bipolar views of a society among the NGOs expressed in dichotomous thinking between 'rural' and 'urban, 'community' and 'state', conflict and order, actor and system.

The fragmentation of NGO social and environmental movements showed that there is no single formula or easy solution to the problems. If the NGOs want to continue their interventionist role to help empower ordinary people and help them gain access to productive resources, they must move beyond their bipolar views of a society to discover the middle ground to search for new meanings, new actors, new issues and to create again and again counter-hegemony movements. This could be done by having abstract development theories assessed and enriched by concrete development practices and *vice versa*. Both theorists and practitioners need to use their own imagination to invent and reinvent what and how best to continue.

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Annual Report of Council

for the year ended 31st March 1998

PATRONS

The Council wishes to express its gratitude to His Excellency the Honourable Sir William Deane, AC, KBE, Governor General of the Commonwealth of Australia, and His Excellency the Honourable Gordon Samuels AC, Governor of New South Wales, for their continuing support as Patrons of the Society.

MEETINGS

Eight Ordinary Monthly Meetings and the 130th Annual General Meeting were held during the year. The Annual General Meeting and five of the General Meetings were held at the Australian Museum. Two General Meetings were held at the Mitchell Library, and one at the Rugby Club.

Special Meeting and Events

April 9th 1997: The Society, the School of French at the University of New South Wales, the Francophone Medical Society and the Australian/French Association of Scientific and Technical Specialists were co-sponsors of a joint meeting at the University of New South Wales at which Mr Fred Blanks delivered an address entitled, "Jeanne d'Arc in music".

April 9th 1997: Members of the Society, Sydney University and descendants of Dr H.G. Douglass, co-founder of the Philosophical Society (precursor of the Society in the 1820s) and co-founder of Sydney University, met at Dr Douglass's grave in Camden, restored largely through the efforts of past-President Dr K.G. Grose. Dame Leonie Cramer, Chancellor of Sydney University unveiled a bronze commemorative plaque.

July 16th 1997: The Society and the Sydney Branch of ANZAAS held a joint meeting at the University of New South Wales at which Mr Dussol of Sofraco P/L conducted a seminar on, "Nuclear propulsion for submarines and surface vessels".

February 10th 1998: The Society was cosponsor with the the Australian Nuclear Association, the Australian Institute of Energy and the Nuclear Engineering Panel of the Institution of Engineers Australia, of a meeting held at The Institute of Engineers, Milson's Point. Topic: "Desalination of Water - needs and opportunities for fossil, nuclear and solar solutions".

March 19th 1998: A very successful Annual Dinner was held in the Holme & Sutherland Room, University of Sydney, at which Professor Gavin Brown, Vice Chancellor of Sydney University, Mrs Brown and 48 Members and guests were present. Professor Brown presented the Society's Awards for 1997 (Royal Society of New South Wales Medal, Clarke Medal (Botany), Edgeworth David Medal) and Archibald D. Ollé Prize, and subsequently gave an Occasional Address.

Meetings of Council

Eleven meetings of Council were held at the Society's Offices at North Ryde.

Dr R. Coenraads resigned his position as Councillor in April due to pressure of business, and Dr K.A. Rickard resigned in November due to illness.

PUBLICATIONS

Journal

Volume 130 Parts 1, 2, 3 and 4 of the *Journal and Proceedings of the Royal Society of New South Wales* were published during the year. The volume carried four peer-refereed research papers on geology, (stratigraphy and structure), palaeontology and physics; ten abstracts of Higher Degree Theses ranging over a wide variety of subjects (including economy, linguistics, medicine, agriculture and physics); and a discussion of nuclear propulsion in marine vessels.

Volume 130 also incorporated the Annual Council Report for 1997/98 and included the Financial Statement, citations for awards for 1997 and biographical memoirs, as well as the Annual Dinner Address by His Excellency the Honourable Gordon Samuels AC, Governor of New South Wales and Vice-Patron of the Society.

Council wishes to thank all referees who volunteered their time and effort. Council received applications seeking permission to reproduce material from the *Journal and Proceedings.*

Bulletin

Eleven issues of the *Bulletin* were published during the year. Council's thanks are extended to the various authors of short articles for their contributions. Very sincere thanks are expressed to Mr Ted O'Keeffe for all his efforts in the preparation of the *Bulletin* throughout the year.

AWARDS

The following awards were made for 1997:-

Royal Society of New South Wales Medal (For achievements in science and service to the Society) - Mr Edward Donald O'Keeffe, Editor of the Society's *Bulletin.*

Clarke Medal (in Botany) - Dr Charles Barry Osmond, Research School of Biological Sciences, Australian National University.

Edgeworth David Medal (For distinguished contributions to Australian science by a young scientist under 35 years of age) - Assoc. Professor Albert Y.H. Zolmaya, Department of Electronic Engineering, University of Western Australia.

Archibald D. Ollé Prize (For the best treatise, or writing or paper on any subject coming within the province of the Society for that year) - Dr Gerrit Neef, Department of Applied Geology, University of New South Wales.

MEMBERSHIP

At 31sth March 1997 membership of the Society was:

Patrons	2
Honorary Members	15
Members	268
Associates, Spouse Members	19
Total	304

The deaths of the following seven members were announced with regret: Mr S.B. Cohen, Mr D.N. Flatt, Dr C.G. Le Fèvre, Prof. J.A. Milburn, Mrs G.F. Proctor, Mr J.A. Shaw and Mrs A.A. Stanton. Fifteen members resigned and ten new members were admitted to the Society during the year.

OFFICE

The Society continued during the year to lease for its office and library a half-share of Convocation House, 134 Herring Road, North Ryde, on the southeastern boundary of the Macquarie University Campus. Council is grateful to the University for continuing the lease. Council greatly appreciates the secretarial assistance rendered by Mrs V. Chandler during the past year. Considerable effort was spent in streamlining office procedures through better use of computer facilities.

SUMMER SCHOOL

After a year's interruption, Council resumed organisation of the Summer School series with the theme, suggested by Dr G.C. Lowenthal, "Progress in Medical Technology - from X-Ray to PET". The school was conducted during 19-20 January 1998 by members of the Royal Prince Alfred Hospital and National Medical Cyclotron , Camperdown, and ANSTO, Lucas Heights. The school was very successful. Fiftysix students enrolled from eight state and fourteen private high schools within New South Wales. Fifteen speakers addressed the students and conducted tours of related clinical departments.

Council heartily thanks the staff of the participating institutions for generously and freely giving their time to the event, and extends their appreciation to Dr Lowenthal as convenor of the school; to Mrs Krysko v. Tryst and other Council members who assisted in organisation; to Dr F.L. Sutherland for assisting with transport; and to Mrs W.C.H. Swaine and Mrs M. Potter for their valuable help with registration and general supervision.

Appreciation for financial assistance goes to Gammasonic Radiological Services Pty Ltd, Five Dock, and to Medical Applications Pty Ltd, Gladesville.

LIBRARY

Acquisition of journal literature by gift and exchange has been continued throughout 1997-98. As in previous years, material from overseas and some Australian literature is sent directly to the Dixson Library, University of New England where it is made available locally, and by photocopies of specific articles, on the inter-library loan network. The remaining Aust-ralian literature is added to the collection of the Head Office Library at North Ryde, which also holds a complete collection of the *Journal and Proceedings of the Royal Society of New South Wales.*

Members of the Society and other authorised readers are welcome to visit the Society's office at North Ryde to consult the Library collection.

Council thanks Mr Karl Schmude and his staff (Mr Bedson and Ms Helen Stokes) for their continuing efficient maintenance of the Society's collection in the Dixson Library. The gift and exchange system is monitored and managed by the Hon. Librarian at Head Office. Library staff of the Dixson Library notifies Head office of any missing issues in the collection and action is taken by the Hon. Librarian.

An accession list of literature received in the Head Office Library is compiled each six months and an appropriate notice appears briefly in the *Bulletin.*

SOUTHERN HIGHLANDS

The Southern Highlands Branch held eight well-attended meetings (see Abstract of Proceedings).

At the Branch's Annual General Meeting on Thursday 6th March 1997, the following were elected to the Branch's Committee for 1997/98:

Chairman	Dr Kenneth McKracken
Vice Chairmen	Mr Roy Perry Ms Christine Staubman Mr Clive Wilmot
Hon Treasurer	Mr Martin Lemann
Hon Secretary	Commander David Robertson

NEW ENGLAND BRANCH

The branch held two meetings during the year (see Abstract of Proceedings).

The branch regretfully reported the tragic accident and death of Professor John Anthony Milburn, who was a strong supporter of the Society and the NE Branch, where he arranged several outstanding evening talks for members. Professor Milburn's obituary was published in Vol. 130 Pts 3/4.

ABSTRACT OF PROCEEDINGS

2nd April 1997. The 130th Annual General Meeting and 1063rd General Monthly Meeting were held at the Australian Museum, Sydney. The President, Dr K.R. Grose was in the Chair and 22 members and visitors were present. The Annual Report of Council and the Financial Report for 1996-97 were adopted. Messrs Wyllie and Puttock were elected auditors for 1997-98.

The following Awards for 1996 were announced and presented by the President:

The Royal Society of New South Wales Medal	Miss P.M. Callaghan
Clarke Medal (Zoology)	Professor K. Rohde
Edgeworth David Medal	Dr P.A. Robinson

Debate over the election of the 1997/98 Council led to Dr Grose passing the Chair to immediate past-President Dr Branagan. Thereafter, the following members were elected:

President: Dr E.C. Potter.
Vice-Presidents: Dr D.F. Branagan, Dr K.L. Grose, Mr J.R., Dr G.C. Lowenthal, Prof. W.E. Smith.
Honorary Secretaries: Dr P.R. Evans, Mrs M. Krysko von Tryst.
Honorary Treasurer: Dr D.J. O'Connor.
Honorary Librarian: Miss P.M. Callaghan.
Members of Council: Dr R.R. Coenraads, Dr M.R. Lake, Dr K.A. Rickard, Dr F.L. Sutherland, Prof. D.J. Swaine, Prof. M. Wilson.
Branch Representatives - New England Mr B. Burns; *Southern Highlands* - Mr H.R. Perry.

Dr. Branagan yielded the Chair to the incoming President, Dr E.C. Potter, who thanked Dr Grose for his hard work during his year as President and for his Presidential Address [A summary of Dr Grose's address was published in *Bulletin* 204].

7th May 1997. The 1064th General Monthly Meeting was held at the Australian Museum. Dr Julia James presented a talk entitled, "Air Quality in Caves".

4th June 1997. The 1065th General Monthly Meeting was held in the Mitchell Library, where Elizabeth Ellis presented a talk upon and a behind-the-scenes view of the libraries pictures collection, covering

"Men and Women of Science in 19th century New South Wales".

2nd July 1997. The 1066th General Monthly Meeting was held at the Australian Museum. Mr F. Blanks addressed the Society on the topic "A definition of music", garnishing his talk with numerous aural examples.

6th August 1997. The 1067th General Monthly Meeting was held at the Mitchell Library. Mr Alan Ventress presented a talk and on-line demonstration on the "Banks papers digitisation project at the State Library of New South Wales 1993-1997".

3rd September 1997. The 1068th General Monthly Meeting was held at The Australian Museum. Mr J. Luikens gave assembled members his thoughts on "Science in Business".

1st October 1997. The 1069th General Monthly Meeting was held at the Australian Museum. Professor Richard B. Frost presented an elevating address entitled, "Engineering problems within operating lifts in high rise buildings".

12th November 1997. The 1070th General Monthly Meeting and presentation of the Clarke Memorial Lecture was held in association with the Geological Society of Australia, Sydney Branch, at the Rugby Club. Dr R.W. Johnson presented a talk entitled, "Volcanic hazards, dangerous calderas, and evolving magmas in island arcs".

Southern Higlands Branch

Thursday 6th March 1997.Dr Lin Sutherland, Principal Research Officer, Directorate of Earth Sciences, Australian Museum, spoke to 50 members and visitors on "Earthquakes and volcanoes in the southern Sydney region".

Thursday 17th April 1997. Mr Andy Macqueen, explorer and biographer, traced explorations by Ensign Francis Barrallier in attempting to find a crossing to the west through the lower Blue Mountains in 1802, and outlined the intrigues in NSW at that time that led to Barallier's survey results going largely unpublished after he was banished from the Colony in mysterious circumstances. 52 members and visitors attended the lecture.

Friday 23rd May 1997. Karine Kelly, former ABC *Quantum* journalist and presenter delivered an address entitled, "Science - a new Dark Age". 76 members and visitors were in attendance.

Thursday 19th June 1997. Mr Fred Blanks AM, spoke to 60 members and visitors (many from local music groups) on the changing definitions through time of what constitutes "Music".

Thursday 7th August 1997. Prof. K.L. Williams, Professor of Biology, Macquarie University and Director of the Australian Proteome Analysis Facility, spoke to 37 members and visitors on the changes that have taken place in Biotechnology since his last lecture to the branch on the human genome. His address was entitled, "Proteomics: a paradigm shift in biology; the birth of a major national facility".

Thursday 18th September 1997. Dr Ronald Lampert spoke to 51 members and visitors on "The archaeology and material culture of the Australian aborigine", based on his excavations at three principal rock shelters on the south coast of NSW, and from contact with the last of the hunter-gatherers in the Western Desert, showing how the technology and economy of the people responded to a changing environment over the last 20 000 years.

Thursday 28th October 1997. Dr Barbara Briggs, Hon. Research Associate, Sydney Royal Botanic Gardens, addressed 41 members and visitors on, "A botanical visit to modern Gondwana", in which she surveyed plant groups found in the southern lands which had a Gondwanan origin.

Thursday 27th November 1997. Prof. Michael Archer, School of Biological Sciences, University of NSW, drawing on discoveries at 'Riversleigh' in NW Queensland, demonstrated to 66 members and visitors in his talk entitled, "Old bones and Australia's future", that many species of Australian faunas, previously thought to have originated as open range animals in fact began in rain forest.

The Southern Highlands Branch Science Award for the Most Outstanding Science Student in Year 11 was won by Miss Claudia Lei, Aurora college, Moss Vale. The prize will cover the expense in her first year of University costs not covered by the Commonwealth Higher Education Scheme (HECS), namely of books and compulsory University Union Fees, payable when the winner commences a science related course at a Tertiary education establishment in 1999.

Thursday, 22nd January 1998. Dr Peter Krug addressed 47 members and visitors on "Lasers, light and modern science", touching on the history of the study of light, the wave-like or particle-like nature of light, the role of light in quantum mechanics and relativity, and the usefulness and applications of light (eg. lasers) in medicine and surgery.

Thursday 19th February 1998. Prof. Michael Dopita, Australian National University, spoke to 78 members and visitors on, "Hubble, the deepest frontier", stressing the intrinsic role played by Australian astronomers in the construction and repair of the Hubble telescope, and explaining the significance to cosmology of stunning images obtained thereby.

New England Branch

Wednesday 16th July 1997. The Branch held a well attended meeting at which the visiting mathematician Peter J. Hilton presented a talk on "Code breaking".

Wednesday 20th August 1997. Professor Martin addessed the meeting on "Conceptualising chronic headaches; medical and psychological perspectives".

FINANCIAL STATEMENTS FOR THE YEAR ENDED 31 DECEMBER 1997

INDEPENDENT AUDIT REPORT TO THE MEMBERS

Scope

We have audited the financial report, being a special purpose financial report of The Royal Society of New South Wales for the year ended 31 December 1997 as set out on pages 2-11. The society's officers are responsible for the financial statements and have determined that the accounting policies used are appropriate for the purpose of fulfilling the Council's financial reporting requirements under its Rules and to meet the need of the Members. We have conducted an independent audit of these financial statements in order to express an opinion on them to the members of the society. No opinion is expressed as to whether the accounting policies used, and described in Note 1, are appropriate to the needs of the members.

The financial statements have been prepared for the purpose of fulfilling the Council's financial reporting requirements under its Rules. We disclaim any assumption of responsibility for any reliance on this report or on the financial statements to which it relates to any person other than the members, or or any purpose other than that for which it was prepared.

Our audit has been conducted in accordance with Australian Auditing Standards. Our procedures included examination, on a test basis, of evidence supporting the amounts and other disclosures in the financial statements, and the evaluation of significant accounting estimates. These procedures have been undertaken to form an opinion whether, in all material respects, the financial statements are presented fairly in accordance with the accounting policies described in Note 1 to the financial statements. These policies do not require the application of all Australian Accounting Standards and other mandatory professional reporting requirements (Urgent Issue Group Consensus Views).

The audit opinion expressed in this report has been formed on the above basis.

Audit Opinion

In our opinion the financial report presents fairly, in accordance with the accounting policies described in Note 1 to the financial statements, the financial position of The Royal Society of New South Wales as at the 31 December 1997 and the results of its operations for the year then ended.

FRANK CLUNE & SON
Chartered Accountants
(Original signed by Alan Puttock, 27/3/98)
ALAN M PUTTOCK
Partner

74 Castlereagh St
SYDNEY NSW 2000

BALANCE SHEET AT 31 DECEMBER 1997

1996		NOTE	1997
	CURRENT ASSETS		
9745	Cash	2	10607
5318	Receivables	3	4810
183	Investments	5	183
0	Inventories		0
400	Other	4	0
15646	**TOTAL CURRENT ASSETS**		15600
	NON-CURRENT ASSETS		
0	Receivables		0
132760	Investments	5	135500
0	Inventories		0
16491	Property, plant & equipment	6	15962
0	Intangibles		0
149251	**TOTAL NON-RECURRENT ASSETS**		151462
164897	**TOTAL ASSETS**		167062
	CURRENT LIABILITIES		
3927	Accounts payable	7	7623
0	Provisions		0
2228	Other	8	2971
2669	**TOTAL CURRENT LIABILITIES**		10594
	NON-CURRENT LIABILITIES		
0	Accounts payable		0
0	Provisions		0
55	Other	8	39
55	**TOTAL NON-CURRENT LIABILITIES**		39
6210	**TOTAL LIABILITIES**		6210
158687	**NET ASSETS**		156429

BALANCE SHEET AT 31 DECEMBER 1996 (CONT.)

1996		NOTE	1997
	EQUITY		
7311	Library Reserve	9	7311
10739	Library fund	10	12325
22350	Trust funds	11	22264
118287	Other accumulated funds		114529
158687	**TOTAL EQUITY**		156429
	Capital and leasing commitments	17	
	Contingent liabilities	18	

(Signed)
E.C. POTTER
President

(Signed)
D.J. O'CONNOR
Hon. Treasurer

ACCUMULATED FUNDS ACCOUNT
For the year ended 31 December 1997

1995		NOTE	1997
(1147)	Operating surplus (deficit)		(3758)
569	Donations and interest to library fund	10	1586
(578)			(2172)
119434	Accumulated funds at the beginning of the financial year		118287
0	Transferred from library fund	10	0
118856			116115
569	Transferred to library fund	10	1586
118287	Accumulated funds at end of the financial year		114529

NOTES TO AND FORMING PART OF THE ACCOUNTS
For the year ended 31 December 1997

1 STATEMENT OF ACCOUNTING POLICIES

These financial statements are a special purpose financial report prepared for use by the council and members of the Society. The council has determined that the Society is not a reporting entity.

The statements have been prepared in accordance with the requirements of the following applicable Accounting Standards and other mandatory professional reporting requirements:

AASB 1002:	Events Occurring After Balance Date
AASB 1018:	Profit and Loss Accounts
AASB 1021:	Depreciation of Non-Current Assets
AASB 1025:	Application of the Reporting Entity Concept and Other Amendments
AASB 1031:	Materiality

No other applicable Accounting Standards or mandatory professional reporting requirements have been applied.

The statements are also prepared on an accruals basis. They are based on historical costs and do not take into account changing money values or, except where specifically stated, current valuations of non-current assets.

The following specific accounting policies, which are consistent with the previous period unless otherwise stated, have been adopted in the preparation of these statements:

(a) Non-Current Investments

Investments are brought to account at cost. The carrying amount of investments is reviewed annually to ensure it is not in excess of the recoverable amount of investments.

(b) Property, Plant & Equipment

Plant and equipment is brought to account at cost or at independent valuation, less, where applicable, any accumulated depreciation or amortisation.

The depreciable amount of all fixed assets is depreciated over their useful lives commencing from the time the asset is held ready for use.

The exception to the above policy is the society's library which is brought to account at its 1936 independent valuation, a more recent valuation not being available.

(c) Comparative Figures

When required by Accounting Standards comparative figures have been adjusted to conform with changes in presentation for the current financial year.

2 CASH

1996		1997
	Included in cash are:	
64	Cash on hand	62
9681	Cash at bank	10545
9745		10607

3 RECEIVABLES

1996		1997
	Included in Current Receivables are:	
2054	Membership subscriptions in arrears	3501
2054	Less provision for doubtful debts	3501
0		0
1986	Debtors for contributions towards printing Journal and Proceedings	1938
3332	Other debtors	2872
5318		4810

4 OTHER ASSETS

1996		1997
	Included in Current Other Assets are:	
400	Prepayments	0

5 INVESTMENTS

1996		1997
	Included in Current Investments are:	
183	Deposits at call	183
	Included in Non-Current Investments are:	
132759	Interest bearing deposits	135500

6 PROPERTY PLANT AND EQUIPMENT

1996		1997
	Included in Property, Plant & Equipment are:	
953	Office equipment and furniture - at cost less depreciation	810
1928	Office equipment - at 1991 valuation less depreciation	1542
13600	Library - at 1936 valuation	13600
10	Pictures - at cost less depreciation	10
16491		15962

7 ACCOUNTS PAYABLE

1996		1997
	Included in Accounts Payable are:	
3927	Sundry creditors and accruals	7623

8 OTHER LIABILITIES

1996		1997
	Included in current Other Liabilities are:	
16	Life Members subscriptions prepaid	16
146	Membership subscriptions paid in advance	75
2066	Journal and Proceedings subscriptions paid in advance	2880
2228		2971
	Included in Non-Current Other Liabilities are:	
55	Life members subscriptions prepaid	39

9 LIBRARY RESERVE

1996		1997
7311	Balance at 1 January	7311
0	Movement for year	0
7311	Balance at 31 December	7311

10 LIBRARY FUND

1996		1997
10170	Balance at 1 January	10739
569	Donations and interest	1586
10739		12325
0	Library purchases and expenses	0
10739	Balance at 31 December	12325

11 TRUST FUNDS

Included in the Trust Funds are:

1996		1997
3018	Clarke Memorial Fund	3027
6788	Walter Burfitt Prize Fund	7202
3237	Liversidge Bequest Fund	3434
8107	Olle Bequest Fund	8601
1200	Dr H.G. Douglass Grave Restoration	0
22350		22264

12 CLARKE MEMORIAL FUND

1996		1997
5000	Capital	5000
	Revenue	
273	Income for year	184
789	Expenditure for year	175
(516)	Surplus (deficit) for year	9
(1466)	Balance at 1 January	(1982)
(1982)	Balance at 31 December	(1973)
3018	Total fund capital and revenue	3027

13 WALTER BURFITT PRIZE FUND

1996		1997
3000	Capital	3000
	Revenue	
529	Income for year	414
595	Expenditure for year	0
(66)	Surplus (deficit) for year	414
3854	Balance at 1 January	3788
3788	Balance at 31 December	4202
6788	Total fund capital and revenue	7202

14 LIVERSIDGE BEQUEST FUND

1996		1997
3000	Capital	3000
	Revenue	
279	Income for year	197
662	Expenditure for year	0
(383)	Surplus (deficit) for year	197
620	Balance at 1 January	237
237	Balance at 31 December	434
3237	Total fund capital and revenue	3434

15 OLLE BEQUEST FUND

1996		1997
4000	Capital	4000
	Revenue	
580	Income for year	494
0	Expenditure for year	0
580	Surplus (deficit) for year	494
3527	Balance at 1 January	4107
4107	Balance at 31 December	4601
8107	Total fund capital and revenue	8601

16 DR H.G. DOUGLASS GRAVE RESTORATION FUND

1996		1997
0	Balance 1 January	1200
3245	Donations and other revenue	1250
2045	Expenditure for year	2450
1200	Balance at 31 December	0

17 CAPITAL AND LEASING COMMITMENTS

1996		1997
0	Capital and leasing expenditure contracted for but *not* already included in the balance sheet	0

18 CONTINGENT LIABILITIES

NIL

DETAILED INCOME AND EXPENDITURE ACCOUNT

For the year ended 31 December 1997

1996		1997
	INCOME	
13351	Membership subscriptions	14319
128	Application fees	158
13479		14477
	Less	
2078	Provision for doubtful debts	1910
11431	Total Membership income	12567
9885	Subscriptions and contributions to Journal publication cost	7446
21316	Total membership and journal income	20013
8157	Interest received	6691
1528	Sale of reprints	209
532	Sale of back numbers	0
70	Sale of other publications	30
0	Research Fees	10
(36)	Annual dinner surplus (deficit) 148	
82	Excursion surplus	0
60	Joint venture with City of Sydney Cultural Council	0
65	Other income	0
31774		27101

1996		1997
	Less EXPENSES	
2760	Accountancy fees	2900
1440	Audit fees	1500
61	Bank charges and government duties	68
654	Depreciation	529
331	Entertainment expenses	282
796	Insurance	784
12709	Journal publication & distribution	10271
244	Miscellaneous expenses	46
(129)	Monthly Meetings deficit (surplus)	292
2039	Newsletter printing & distribution 2531	
746	Postage	625
1061	Printing & stationery	621
2000	Rent	2000
25	Repairs	8
7322	Salaries	7462
397	Superannuation contributions	448
465	Telephone	492
32921		30859
(1147)	**DEFICIT** for the year	(3758)

CITATIONS FOR AWARDS

THE SOCIETY'S MEDAL FOR 1997

Edward Donald O'Keeffe

The Society's Medal is given for advancement of science and contributions to the Society.

Edward Donald O'Keeffe graduated from the University of Sydney in General Science with a Diploma in Education. This was supplemented by a MSc from Macquarie University. After a few years teaching mathematics at High Schools and the Sydney Teachers College, he joined the staff of the Mathematics Department at Macquarie University in 1969. He is currently a Senior Lecturer there and Assistant Head of the School of Mathematics, Physics, Computing and Electronics.

Ted is the principal author of a textbook entitled, "Understanding Computer Programming". Following an appointment as an Adjunct Professor at the University of Arizona, he published a report on "Reform Calculus: experience in the USA". He has been very active in administration at Macquarie University, for example as a member of the Council, as a member of the Academic Senate working parties and of the Undergraduate Studies Committee.

Ted O'Keeffe has outstanding achievements as a professional scientist, not only in University administration, but also in outside bodies, for example the New South Wales Board of Studies Syllabus Committee, as an examiner for HSC mathematics and as a consultant for the Australian International Development Assistance Bureau. Other activities have been with the Macquarie University Continuing Education Program, the Australian Mathematical Society and the Mathematical Association of New South Wales. He joined the Royal Society of new South Wales in 1984 and was a member of Council in 1985 and from 1990 to 1993. His major important work for our Society is as Editor of the Bulletin, a task that he has carried out with skill and efficiency since 1992.

Mention must be made of Ted O'Keeffe's outstanding sporting successes. He has a Blue in Golf from the University of Sydney and in squash from Macquarie University. He has represented New South Wales in squash and was the Australian Universities champion and the Number One player in the combined intervarsity squash team in 1968. He was the first intervarsity champion in any sport from Macquarie University. He has also played grade A tennis. Surely he is the only mathematician with a double Blue. His continued efforts in several spheres at Macquarie University are marked by the establishment of the Ted O'Keeffe Scholarship, which has been referred to as the Macquarie version of a Rhodes Scholarship.

Ted O'Keeffe's many achievements, especially as a highly respected teacher of mathematics, and his continuing sterling service to the Royal Society of New South Wales surely make him a very worthy recipient of the Royal Society/s Medal for 1997.

THE CLARKE MEDAL (BOTANY)

Professor Charles Barry Osmond

The Clarke Medal is awarded for distinguished work in the natural sciences done in, or on, the Australian Commonwealth and its territories.

Professor Charles Barry Osmond is an eminent botanist and plant physiologist and is currently the Director of the Research School of Biological Science at The Australian National University. It is pertinent to note that he received the Edgeworth David Medal of the Royal Society of New South Wales in 1974. He is a graduate of the University of New England and of the University of Adelaide, and he has had research appointments overseas, for example in the USA, Germany and Japan. His efforts at the Desert Research Institute, Reno, Nevada, led to the restoration of biological programs there.

Professor Osmond's research in plant physiology and biochemistry has ranged from environmental aspects to the bioenergetics of photosynthesis. His early field studies in western New South Wales on ionic relations and the metabolism of saltbushes (Atriplex) were the basis of collaborative work which discovered a new pathway of photosynthetic metabolism. Further field work lead to the explanation of how Prickly Pear became established and recent work with colleagues has elucidated the unusual metabolism of Prickly Pear that explains how Cactoblastis is an effective controlling agent. Perhaps his prime research has been chemical studies of metabolism in succulent plants and recent work on photo inhibition, which is the games plants play when exposed to excess light. Professor Osmond has a most impressive record of publications, including the editorships of ten books, and he has received several large research grants.

In addition to associations with various scientific societies in five countries, he has editorial responsibilities with botanical and plant sciences journals. Other diverse activities include reviewing research papers, membership of national and international groups and participation in exchange programs. He has been President of the Australian Society of Plant Physiologists and an organiser of a Gordon Conference.

It is abundantly clear that Professor Osmond's impressive contributions to several areas of research make him a most worthy recipient of the Clarke Medal for 1997.

THE ARCHIBALD D. OLLÉ PRIZE FOR 1997

Dr Gerrit Neef

The Archibald D. Ollé Prize is awarded from time to time at the discretion of the Society's Council to the member of the Society who in any year submits to the Society the best treatise, or writing or paper on any subject coming within the province of the Society for that year.

Council is pleased to award the prize for 1997 to Dr Gerrit Neef for his paper entitled, Stratigraphy and Structure of an outboard part of the forearc of the Hikurangi Margin, North Wairarapa, New Zealand', which was judged the best paper published in the Journal and Proceedings during 1997.

Dr Neef, who received his secondary education in England, graduated in 1957 with a BSc (Hons) in Geology from University College, London. After several years of industrial experience in England, northern Canada and New Zealand, in 1967 Dr Neef gained a PhD in Geology from Victoria University in Wellington, New Zealand.

The same year, Dr Neef accepted a Lectureship at the W.S.S. and L.B. Robinson University College in Broken Hill, western New South Wales. He was promoted to Senior Lecturer in 1976 and, on closure of the College in 1983, he accepted a transfer to the Department of Applied Geology at the University of New South Wales, Kensington. Although now retired from that position, Dr Neef has maintained close links with the Department of Applied Geology as he continued his research.

Dr Neef has been a Member of the Royal Society of New South Wales since 1989, and is a Member of the Geological Society of Australia and a Fellow of the Geological Society of London.

Dr Neef's research, largely in the field, has ranged from the ancient terrains of western New South Wales, centred on Broken Hill, to the active crustal plate margin of the southwestern Pacific Islands, of which the Wairarapa region, on the northeast coast of the North Island of New Zealand, is part. This range of interests is exemplified by the fact that Dr Neef published a primary study of Devonian , that is 350 million year-old rocks in the region of Mootwingee, north of Broken Hill in the first part of the Society's journal in 1997, then, in the second half of the journal in the same year, the study of the 80 million years and younger rocks in the Wairarapa region of the North Island of New Zeland that is the subject of this prize.

To misuse a popular TV phrase, Dr Neef likes to go where no man has gone before. He has been willing and able to examine what geologists might regard as the extreme limits of the suite of rocks that comprise the state of New South Wales. [I apologise to any New Zealanders in the audience, but after all the North Island of New Zealand is a fragment of the earth's crust that just happened to break away from New South Wales a mere 80 million years ago]. The terrains in which Dr Neef has worked are strucuturally very complex and it is to Dr Neef's credit that his careful attention to detail in the field has enabled him to contribute such worthwhile analyses of such diverse regions either side of the Tasman.

Without doubt, Dr Neef is a worthy recipient of the Archibald D. Ollé Prize.

THE EDGEWORTH DAVID MEDAL FOR 1997

Associate Professor Albert Z.H. Zomaya

The Edgeworth David Medal is awarded for distinguished contributions to Australian science by a scientist under the age of thirty five.

Albert Zomaya graduated from the University of Kuwait with a Bachelor of Engineering in 1987 and then completed his PhD in the Department of Automatic Control and Systems Engineering at the University of Sheffield in 1990. Since then, he has worked as a Lecturer in the Department of Electrical and Electronic Engineering at the University of Western Australia and has been quickly promoted first to Senior Lecturer and then to Associate Professor in 1996. He has held visiting appointments at the University of Waterloo and the University of Missouri Rolla.

His research interests are in parallel algorithms and architectures of computers. These questions are at the foundations of the application of modern computer science and the theory and experiment are often highly technical. Associate Professor Zomaya is tackling several fundamental areas of parallel computing and its applications in his research.

There are several issues related to parallelisation that do not arise in ordinary sequential programming. One of the most important is task allocation, that is the breakdown of the total workload into smaller tasks assigned to different processors and the proper ordering of the tasks is a formidable problem and essential if the best use is to be made of available computing power. The task of finding the best possible solutions typically requires prohibitive amounts of computing, but optimisation algorithms can be used to solve a wide class of problems that arise in the design and operation of parallel computing environments. Some unorthodox approaches such as genetic algorithms, neural networks and simulated annealing are attractive and accessible with fast parallel computers.

During the operation of a parallel processing system, a faulty component must be isolated and replaced by an operational one to avoid crashing the system. The time constraint in this application is obvious since it is not much use finding the problem after the system has been crashed. A real-time system in the shape of a mobile robot that carries its own computing system on board is being constructed to test developed algorithms. Heuristic techniques are being applied more generally to handle the computationally intensive algorithms in robotics.

Associate Professor Zomaya has published three books, edited two books and published over 40 research papers in international journals. He has been a co-investigator on a successful large ARC grant for $150 000. He gave an invited keynote address at the International Conference on System Sciences in Hawaii in 1997 and has given invited talks at several universities in the USA, Canada and Asia. He is editor of a number of international journals in computing. He has already supervised three successful PhD students in neural networks and parallel computation and has another three currently under his supervision.

Albert Zomaya is a worthy recipient of the Edgeworth David Medal.

Biographical Memoir

CATHERINE GUNN LE FÈVRE
1909-1998

Catherine Gunn Le Fèvre was born in Glasgow on the first of November 1909, the only daughter of the three children of Christine and Charles Tideman.

She studied science at University College London where she met and, in 1931, married Raymond James Wood Le Fèvre, then a lecturer in organic chemistry. In Le Fèvre's own words from his diary, Cathie at this time was "always cheerful, lively, ready with relevant comments on current or local affairs, full of conversational topics, of repartee, energy and vigour". These words described her well all through life. The Le Fèvres were an exceptional couple and theirs was to be a long and particularly happy marriage.

In the late twenties Cathie held positions as a teacher and a microbiologist but soon joined Ray in what became a life-long and brilliant research collaboration. Together they pioneered methods for determining molecular polarisabilities from measurements of the Kerr effect (electrically induced double refraction). They interpreted the polarity and polarisability of molecules to solve fundamental questions of electronic behaviour and molecular geometry. The early stages of this work took place in what was undoubtedly a period of greatness for UCL Chemistry. Luminaries such as Robert Robinson, Christopher Ingold (both later knighted), Frederick Donnan, Edward Hughes were their mentors and colleagues. In time, we in Australia were to be the fortunate beneficiaries of these illustrious associations.

Their first child, Ian, was born in 1937 and Nicolette in 1940. World War II had broken out and Cathie experienced difficult and lonely years raising a young family in war-torn London. For the major part of the war, Ray Le Fèvre served overseas with the RAF and the RAAF as Scientific Adviser, posted in the Far East and then Australia, returning to Britain in December 1943.

It was less than three years later that the family moved to Australia when Ray (evermore the Prof.) accepted the position of Professor of Chemistry at the University of Sydney. Together, the Prof. and Cathie set about re-establishing their laboratory and building up a strong research group. Their work brought world recognition. The Prof. was elected as a Fellow of the Royal Society in 1959; Cathie was awarded the degree Doctor of Science from the University of London in 1960. The Le Fèvres were a superb team both professionally and personally. A whole generation of postgraduates fortunate enough to be part of the Le Fèvre group learnt first hand from Cathie the intricacies of the physical techniques and analytical procedures she and Ray had devised. The encouragement she gave when the time came for each of us to deliver our first research seminar was as warm as it was instructive. So many graduate students were frequent recipients of Cathie's generosity and her wise counsel whether in the laboratory or her Northbridge home we in the group were made to feel part of the family.

Cathie was a high-spirited woman who held strong views on both scientific and social issues - these views were the more convincing because of her remarkable intellectual energy and insight. This energy was expressed in a wide range of interests. Although Cathie could turn her hand to concreting over a back garden (and she did), her activities were largely intellectual and artistic. Particular mention deserves to be made of her considerable ability and talent as an artist. As well, she played a mean hand at bridge.

Cathie was active in the Sydney University Settlement and other University charities. She was the first woman to be elected to the Council of the Australian Academy of Forensic Sciences, a venue which afforded her many opportunities to cross intellectual swords with the legal profession. This is something Cathie gained a taste for in earlier days, the sixties and seventies, when she was in the thick of the debates on Drug Dependence and Law Enforcement. She co-authored a monograph on the subject. For many years she was a correspondent for the Lancet.

Other links with the learned societies included: The Royal Society of New South Wales, The Royal Australian Chemical Institute and the Australian Academy of Science. She joined the Royal Society of New South Wales in 1961 and maintained a close and generous interest in the Society's activities until 1997, when she attended the Annual Dinner. In memory of her beloved Ray, Cathie established in 1986, The Le Fèvre Young Researchers in Chemistry Prize. This is awarded annually under the auspices of the Academy, and is regarded as a major prize in chemistry research in Australia. Further, Cathie became a Senior Donor to the Academy's Foundation for Science, and was actively involved in the development and promotion of the Primary Investigations Science Program for the early school years.

Cathie had a passion for encouraging young people, especially women, to undertake a career in science. She initiated a Women in Science Program; she established the R.J.W. Le Fèvre Scholarships for Postgraduate Women in Chemistry to enable the recipients to attend conferences overseas; and she endowed the prestigious C.G. and R.J.W. Le Fèvre Postgraduate Student Lectures under the auspices of the Sydney University Chemical Society - Cathie was a Life Member.

Such support for activities of the Chemistry School at Sydney were mirrored by generosity towards Macquarie University and followed the links forged there by her husband. There may well be other benefactions; Cathie did not broadcast such matters.

There were sad losses in Cathie's life - the tragic drowning of her son Ian in 1977 and the death, almost 12 years ago, of her beloved husband. But Cathie embraced life. She gave so generously of herself. Her brilliant, alert, vital, blue eyes were so expressive and said so much about the great woman she was.

Fiercely loyal, she gave love and support to those near to her and especially to her family of which she was so proud. Cathie is survived by her daughter Nicolette, son-in-law Max, four grandchildren and three great grandchildren.

R.S. Armstrong
M.J. Aroney

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New Molecular Receptors for Small Molecules and Ions

LEONARD F. LINDOY

Abstract. New macrocyclic and cage-like receptors have been synthesised. The host-guest complexation behaviour of these species with metal cations and, in one instance, organic guests has been investigated using a range of physical and computational techniques. Emphasis in these studies has been given to the development of systems showing selective host-guest complexation behaviour.

Keywords: heavy metal, selectivity, host-guest, macrocycle, cage.

INTRODUCTION

Although the recognition of ionic and molecular species is a unifying theme throughout nature's chemistry, it is only in comparatively recent times that a substantial effort has been expended on the design and synthesis of synthetic systems that might exhibit comparable recognition behaviour (Izatt *et al.*, 1991) (Martell *et al.*, 1994). In this paper, selected results from our ongoing studies are presented illustrating how organic systems have been designed to recognise, and in some cases discriminate for (or against), both individual transition metal ions as well as small neutral molecules.

Metal-Ion Recognition

It is now around one hundred years since Alfred Werner first elucidated the nature of metal-ion complexes. Despite this, and the innumerable studies that have taken place in the area since Werner's time, it still often remains rather difficult to predict the metal binding preferences of individual binding sites, especially when mixed donor atom patterns and/or irregular coordination site geometries are involved. It is worthy of note that sites of these latter types tend to be the rule rather than the exception in biochemical systems. Apart from gaining a fuller understanding of the role of metals in biology, there are a host of more practical reasons for undertaking studies of metal-ion recognition. An understanding of the area has implications for each of the following: the design and construction of sensing elements for metal-ion detection and measurement, the design of metal-ion separation processes in a range of industrial (including mining) applications, the control and clean-up of heavy metal pollution as well as for medical use in the treatment of heavy metal poisoning in humans. Laboratory applications include chromatographic separations and a range of classical metal analysis procedures.

How does one tackle the problem of designing new reagents for metal ions of interest? First there are some long established guidelines that one can heed. The HASB (hard acid/soft base) proposal of Pearson (Pearson, 1990), along with the older 'a' and 'b' classifications (Ahrland *et al.*, 1958; Ahrland, 1996) provide a general guide as to what donor types will show especial affinities for what metal ions. This is a useful guide, particularly when single donor atom types are present; however, in the author's experience these classifications are not without problems (the unexpected low affinity of thioether groups for some soft metals but not others provides an example). The Irving-Williams stability order (Irving and Williams, 1953), also proposed by the Australians D. P. Mellor and L. Maley from work performed at Sydney (Mellor and Maley, 1947), in many instances also aids the prediction of the relative stabilities of the divalent metal complexes of metals from the latter half of the first-row transition series (namely, from manganese to zinc).

For some time our research has involved an investigation of the recognition behaviour of mixed donor macrocyclic ligands towards a range of industrially important metal ions such as cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II). (Ahearn *et al.*, 1996). A focus of our investigations has been the development of strategies for achieving discrimination between these ions but, more importantly, for understanding the nature of such discrimination when it is achieved. The use of macrocyclic ligands in such studies has two major advantages. First, it provides another parameter - the macrocyclic ring size - that can be employed in the tuning of a given ring for a metal ion of interest. Secondly, because of the inherent configurational restrictions associated with their cyclic nature, macrocyclic ligands tend to give rise to simpler solution speciation patterns for metal complexation than do their open chain analogues (Lindoy, 1989). Indeed, the former frequently yield simple 1:1 (metal:ligand) complexes as the only complex species present in solution. Such absence of complicated speciation considerably aids the investigation of stability patterns.

A very wide range of mixed-donor cyclic systems has now been investigated, with typical examples being illustrated by the four- and five-donor structures **(1)** and **(2)***, where X and Y are nitrogen, oxygen and/or sulfur donors. It has proved advantageous in our studies to employ cyclic systems such as these that are of intermediate flexibility. This tends to limit the number of ligand conformations/configurations possible on binding to a metal, while still permitting ready uptake (and/or loss) of the metal with respect to the macrocyclic ring. Mixed donor sets are also often an advantage in this regard since they tend to reduce the very high kinetic and thermodynamic stabilities that are characteristic of, for example, many all nitrogen donor macrocyclic systems. Such high stabilities generally cause difficulties when undertaking solution equilibrium studies using conventional techniques.

Small molecule recognition

The strategies for designing synthetic receptors ('hosts') for binding small molecules ('guests') to a large degree parallel those discussed so far for obtaining new metal-ion receptors. However, in the former case, more complex-shape recognition may need to take place and covalent host-guest

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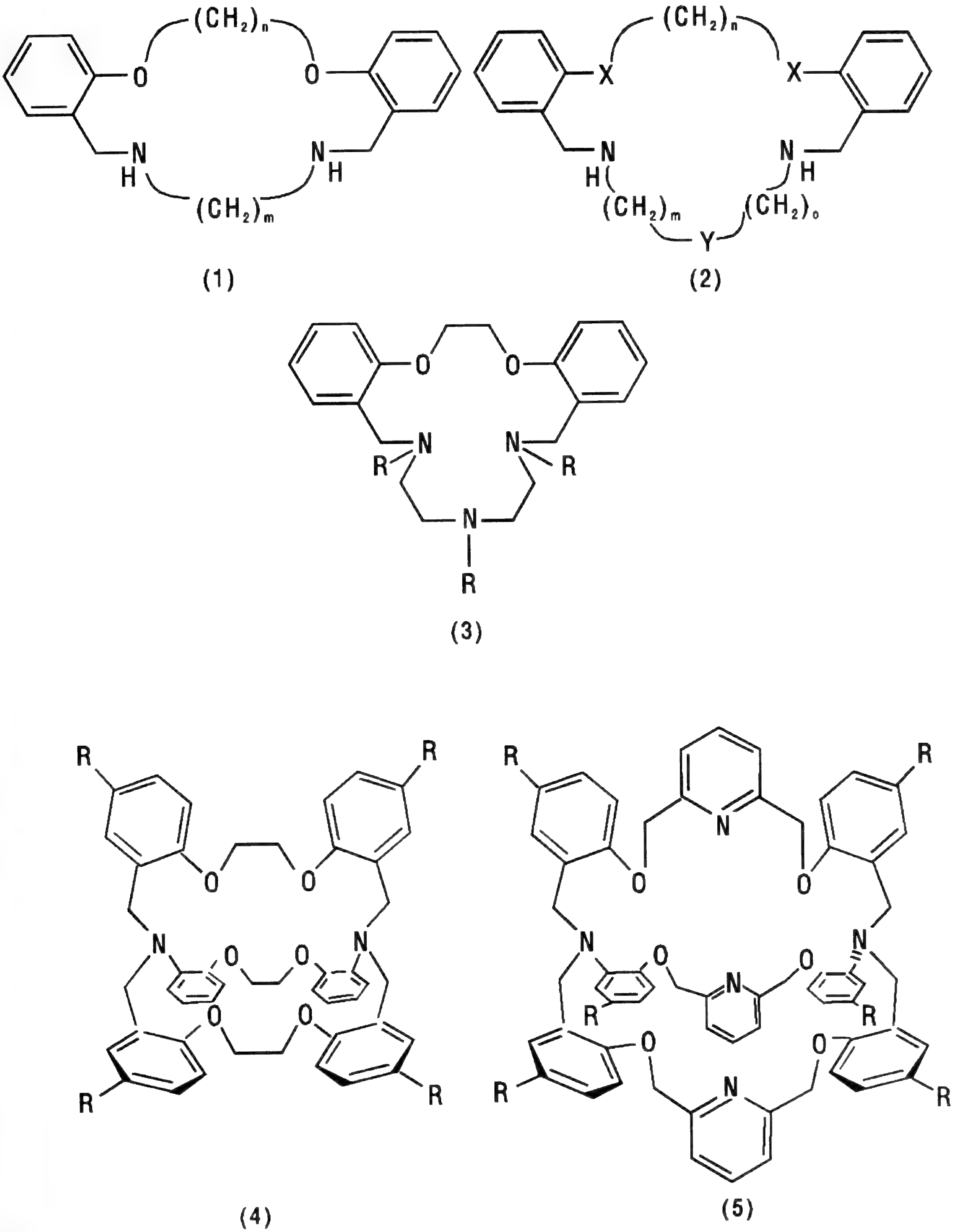
* Numbers in parentheses and in bold type here and in the rest of the text refer to the molecular structures illustrated in Fig. 1.



(1) (2)

(3)

(4) (5)

Fig. 1. Structures of Molecular Receptors

linkages are no longer appropriate if reversible binding is to be achieved. Weaker intermolecular forces (including hydrogen bonds-interactions and van der Waals interactions) between host and guest now become the order of the day (Whitesides *et al.*1995).

VARIATION OF STRUCTURAL PARAMETERS TO ACHIEVE METAL-ION RECOGNITION.

In our studies we have employed a general strategy for achieving metal-ion recognition that has involved the regular variation of structural parameters within a series of macrocyclic ligands of related type (Adam and Lindoy, 1992). More specifically, we have employed systematic variation of the macrocyclic ring size, the donor set present and/or the degree of substitution of the parent ring structure to 'tune' the affinity of a given ring type for a chosen metal ion. It is convenient here to exemplify each of these approaches separately; however, in many instances it is clearly advantageous to use variations of all three parameters simultaneously in order to maximise metal ion recognition. This is perhaps best illustrated by considering the process as one in which one moves stepwise within a ligand 3D structural matrix for which the axes are: macrocycle ring size, donor set type and degree of ring substitution. That is, stepwise movement within the matrix is used to maximise recognition behaviour.

VARIATION OF MACROCYCLIC RING SIZE

The variation of macrocyclic ring size in order to provide a macrocyclic cavity that matches the radius of a particular metal ion has long been employed (Lindoy, 1989) as a strategy for obtaining selectivity for individual metals based on their respective ionic or covalent radii. In general, strongest metal-ion binding occurs when the ligand's cavity best matches the radius of the bound metal ion. Despite this, it needs to be noted that such an approach is often far from straight forward. For systems that are not completely rigid, some contraction or expansion of the macrocyclic cavity may occur to meet the dictates of the bound metal which, in any case, may choose not to fully occupy the macrocyclic cavity.

In an earlier study, we employed the above 'hole-size match' strategy to obtain metal-ion recognition. Thus, X-ray structural analyses (and associated molecular mechanics modelling) indicated that the 14 - to 17-membered rings (**1**; n = m = 2), (**1**; n = 2, m = 3), (**1**; n = 3, m = 3) and (**1**; n = 2, m = 4) yield nickel(II) complexes of type $[NiLX_2]$ (X = Cl or Br) in which the metal ion occupies the respective macrocyclic cavities, with the X groups occupying trans (axial) positions such that each complex has a similar pseudo octahedral coordination geometry (Adam, Leong *et al.*, 1988).

The structural studies coupled with hole size calculations indicate that the 16-membered ring makes available a near ideal coordination cavity for this ion in its high-spin state. Accordingly, the respective stability constants (log *K* values corresponding to the formation of 1:1 complexes) for the interaction of this ligand series with nickel(II) in 95% methanol are 3.7 (14-membered ring), 5.4 (15-membered ring), 5.8 (16-membered ring) and ~3.5 (17-membered ring). Not unexpectedly, the rate constants for the dissociation of these complexes in acid follow the reverse order to these log *K* values.

A second strategy introduced by us uses variation of macrocyclic ring size to induce what we term 'dislocation discrimination'.

This depends on an abrupt structural change in coordination behaviour being induced for one metal ion relative to another as the macrocyclic ring size is progressively altered. At the point of dislocation, the coordination geometry change may lead to an enhanced stability differential (or unusual stability order) between the complexes of the respective metals. This is best illustrated by means of an example.

An investigation of the formation of the the zinc(II) and cadmium(II) complexes of the 16- to 19-membered macrocycles of type (**2**; X = O, Y = NH) (Adam, Dancey *et al.*, 1988; Adam *et al.*, 1994) revealed that the relative stabilities of the 1:1 zinc(II) and cadmium(II) complexes in 95 percent methanol followed the overall pattern shown in Table 1. Thus, the 17- and 18-membered ring species yield cadmium(II) complexes which are in each case more stable than the corresponding zinc(II) complexes. However, for both 19-membered ring species this order is reversed. The crystal structures of $[Zn(NO_3)_2L]NO_3$ and $[Cd(NO_3)_2L]$, where L = (**2**; X = O, Y = NH, n = m = o = 2), show that all five donors of the macrocyclic ligand are bound to the metal in the case of the cadmium(II) complex while, for the zinc(II) species, the ether oxygens do not coordinate. The relative thermodynamic stabilities of these complexes [the cadmium(II) species is more stable than the zinc(II) species] is in accordance with similar structures to those found in the solid state persisting in solution - with donation from the ether oxygens appearing to make little (if any) contribution to the stability of the zinc(II) species. In contrast, a contribution does appear to be made in the case of the cadmium(II) complex. The overall stability pattern also suggests that the above situation (non-coordination of the ether donors in the case of the 17-membered zinc complex) also occurs for the corresponding18- and 19-membered zinc(II) complexes.

Inspection of the log *K* values for the respective cadmium(II) complexes (Table 1) accords with the presence of a structural 'dislocation' occurring between the complexes of the 18- and 19-membered rings. Inspection of molecular models suggested that the observed dislocation may reflect a change from coordination to non-coordination of the ether oxygens on passing from the complex of the 18- to that of the larger 19-membered ring. In accordance with this, an X-ray structure determination of the cadmium(II) nitrate complex of this latter ring shows that non-coordination of the ether functions does occur in the solid state.

It should be noted that a similar stability pattern is observed for the related zinc(II) and cadmium(II) complexes of the analogous 17- to 19-membered, N_3S_2-donor macrocycles of type (**2**; with X = S, Y = NH)

Table 1. Log *K* values (ML^{2+}) for the zinc(II) and cadmium(II) complexes of the N_3O_2-donor (X = O, Y = NH) macrocycles of type (**2**) in 95% methanol, $I = 0.1$ (Et_4NClO_4), at 25°C.

Macrocycle	Ring size	log *K* values Zinc(II)	Cadmium (II)
2; n = m = n = 2	17	7.5	8.5
2; n = 2, m = 2, o = 3	18	7.1	7.9
2; n = 2, m = 3, o = 3	19	6.6	5.3
2; n = 2, m = 2, o = 4	19	6.0	5.0

(Adam, Arshad *et al.*, 1994). That is, the 17- and 18-members of this series yield cadmium(II) complexes which are once again more stable than their zinc(II) analogues. While, as before, for the complexes of the 19-membered ring (**2**; X = S, Y = NH, n = 2; m = o =3), this order is reversed.

In summary, for both the N_3O_2- and N_3S_2-donor ring systems discussed above, it can be seen that the occurrence of a structural dislocation in the formation of the cadmium(II) complexes of the respective 19-membered rings, is reflected by a change in the metal recognition properties of these ligands (19-membered: cadmium < zinc) relative to their smaller ring analogues (17- and 18-membered: zinc < cadmium).

Variation of Donor Atom Set

As mentioned earlier, donor set variation has traditionally been employed in the design of ligands for the selective binding of metal ions of interest. In our metal discrimination studies we have also employed such a procedure; for example, we have employed donor atom variation within the 17-membered rings of type **(2)** in which X and Y were varied in a regular manner from NH to O to S. In one study of this type, it was our aim to maximise discrimination for silver(I) over lead(II) - two metals that are found together in nature.

The thermodynamic stabilities of the complexes of these metals were again measured potentiometrically in 95 percent methanol (I = 0.1, Et_4NClO_4) as the nature of X and Y in **(2)** was varied in a stepwise manner. The results are summarised in Table 2.

In the initial log K determinations, the values for the complexes of the 'parent' (17-membered) N_3O_2-donor ligand (**2**; X = O, Y = NH) indicated that little discrimination was evident between the complexes of the above metal ions (the Δlog K for the silver complex over the lead complex is less than an order of magnitude). On moving to the related 17-membered N_5-donor system (**2**; X = Y = NH), little improvement was observed even though the absolute log K values are higher in both cases. However, on moving to the system with X = O, Y = O, then discrimination for silver(I) increases (even though the overall values are lower). It is clear from this that the silver(I) ion is more tolerant towards a $NHCH_2CH_2XCH_2CH_2NH$ bridge(where X = O, in this case) than is lead(II); perhaps paralleling the well known tendency for silver(I) to form a simple

Table 2. Effect of donor set on log K values on silver(I)/lead(II) discrimination for the complexes (ML^{n+}) of the 17-membered ring (**2**, n-m-o=2) in 95% methanol, I = 0.1 (Et_4NClO_4), 25°C.

Ligand	Silver(I)	Lead(II)	Δlog K
2; X=S, Y=S (S_2N_3)	12.4	~3.1	~9.4
2: X=S, Y=O (S_2N_2O)	10.3	-	~7.3
2; X=S, Y=NH (S_2N_3)	~11.7	8.0	~3.7
2; X=S, Y=NH (O_2N_2S)	8.6	4.5	4.1
2; X=O, Y=O (O_3N_2)	7.1	5.5	1.6
2; X=O, Y=NH (O_2N_3)	8.7	8.1	0.6
2; X=Y=NH (N_5)	10.3	9.4	0.9

diammine species.

Silver(I) is a soft metal ion while lead(II) is borderline (Ahrland, Chat and Davies, 1958) and hence it was reasoned that substitution of a thioether group for an ether group might further enhance the stability differential between the complexes of these ions. This was clearly found to be the case (Table 2). The stepwise replacement of sulfur for oxygen or nitrogen in positions X and Y of **(2)** results in a steady increase in the $\Delta\log K$ value in favour of silver. For the final compound in the series, namely the N_2S_3-donor ligand (which it is noted also contains a heteroatom other than NH in the X-position), the stability difference is now ~10^9!

The above result provides a powerful illustration of the effect that a 'tuning' strategy, involving the systematic variation of just one structural parameter (in this case the donor atom set), may have on achieving metal-ion discrimination of a high order.

X-ray diffraction structure determinations on the solid silver complexes of type $[AgL]NO_3$ [where L is a 17-membered ring of type **(2)** with X = S, Y = O (Adam, Baldwin *et al.*, 1994; X = S; Y = NH (Kallert and Mattes, 1991); and X = S, Y = S (Kallert and Mattes, 1992) and the lead complex $[PbL(ClO_4)_2]$ [where L = **(2)**, X = S, Y = NH] (Adam, Baldwin *et al.*, 1994) clearly reflect the results obtained from the solution stability studies. Namely, while all three silver complexes have similar structures in which the ligand 'wraps' tightly around the central metal ion such that all donor atoms of the respective ligands bind to silver to yield five-coordinate geometries, in the case of the lead complex the structure shows that macrocycle binding is much weaker. The cyclic ligand does not 'wrap' around the lead(II) ion but rather coordinates in an approximately planar fashion in which particular metal-donor atom contacts are somewhat elongated. Further, the coordination number in this complex is expanded to seven by the coordination of two perchlorate anions in 'axial' positions.

The difference between the X-ray structures of the lead complex and the silver complexes, thus accords with a weaker binding of (**2**; X = S, Y = S) in the case of the lead complex - a situation that fits well with the stability trends summarised in Table 1.

RING SUBSTITUTION

Effect of Ring Substituents

In an ongoing study, the effects of N-methylation and N-benzylation of the nitrogen sites of the parent 17-membered, N_3O_2-donor macrocycle (**2**; X = O, Y = NH) on the thermodynamic stabilities of the corresponding complexes of nickel(II), copper(II), zinc(II), cadmium(II), lead(II) and silver(I) have been determined under the conditions mentioned previously. The results are illustrated in Table 3. For the first five metal ions, the presence of the substituents [see

Table 3. Effect of N-substituents on Log *K* values (ML^{2+}) for the complexes of (**3**) with the metal ions shown in 95% methanol, *I* = 0.1 (Et_4NClO_4), 25°C.

Ligand	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Ag(I)	Pb(II)
1; R = H	7.6	10.0	14.4	7.5	8.7	8.7	8.1
1; R = CH_3	<3.5	<3.5	-	5.1	6.1	10.3	6.6
1; R = Benzyl	<3.5	<3.5	-	~3.5	~3.5	9.3	4.3

(3)] leads to metal complexes of lower stability, with, in general, the presence of the bulky benzyl groups causing a larger reduction than the corresponding N-methyl substituents. This is the expected situation, reflecting the presence of steric hindrance to metal coordination. However, somewhat surprisingly, in the case of silver(I) a similar effect is not observed - there is even a small increase in stability for the complex of the benzylated ligand derivative with this ion.

In effect, the above behaviour amounts to the selective 'detuning' of the parent ring by N-alkylation for all the divalent metals, but not for monovalent silver(I). While the origins of this behaviour remain uncertain, they may parallel a previously documented observation that tetra-N-methylation of the N_4-macrocycle, cyclam, results in a product that stabilises the monovalent oxidation state of copper relative to its divalent state (Golub *et al.*, 1995). Further work is in progress in our laboratory to confirm or otherwise whether this suggested parallel is in fact the case.

Overall, the discussion so far illustrates how macrocycle hole size, donor set type and degree of substitution can all be employed to influence markedly the discrimination behaviour of a macrocyclic ligand. Once again, it is stressed that the opportunity exists to vary more than one of these parameters during the tuning process, leading to 'synergisticly'enhanced discrimination in suitable cases.

MOLECULAR CAGES

We have also been involved in the design and synthesis of new 'cage' structures that contain three dimensional cavities for selectively binding 'guest' metal ions or small molecules. Relative to simple ligands, cages such as **(4)** are potentially able to present a more 'defined' cavity to an incoming guest of the above type. Namely, complementarity (both steric and electronic) with the guest ion or molecule is in principle able to be obtained more readily due to the three dimensional nature of the cage structure. This is an important advantage in turns of designing such systems for selectively binding a guest of interest.

In our initial studies, we observed that cages of type **(4)** are generally poor coordinating agents for metals such as the alkali metals (Atkinson *et al.,* 1996). From structural studies (Atkinson *et al.,* 1994) coupled with a molecular modelling investigation (that included DFT calculations) (Atkinson and Lindoy, 1998), the reason for the poor affinity of such cages for alkali metals has been elucidated. It is clear that these systems do not have an *endo* arrangement of the lone pairs on the nitrogen caps [as is illustrated by **(3)**] but rather an *exo-exo* arrangement is dictated by steric factors and this results in the lone pairs being orientated away from the central cavity. In turn, this has the consequence of forcing the benzyl -CH_2- groups into the central cavity such that its volume is much reduced; the cavity is no longer large enough to accommodate an alkali metal ion.

As an aside, when one or two of the aromatic ring-containing 'straps' linking the terminal nitrogen atoms of the N_2O_6-cage (**4;** R = *t*-Bu) was replaced by an aliphatic strap of type-$CH_2CH_2OCH_2CH_2OCH_2CH_2$-, then uptake of individual alkali metals was observed to occur (Adam *et al.*, 1998). This behaviour is a direct consequence of the additional flexibility present in the new derivatives. This enables them to achieve *endo-endo* arrangements of the nitrogen bridgeheads (White and Skelton, 1998), with a concomitant increase in the cavity size available for binding an alkali metal ion. A series of solvent extraction experiments ($H_2O/CHCl_3$) involving the differential extraction of alkali picrate salts is now complete. These indicated that, under the conditions employed, only the cages incorporating the aliphatic 'straps' were effective extractants of alkali metal picrates into the chloroform phase.

Small Molecule Recognition

As a direct extension of the above studies it was decided to expand the available cavity in the N_3O_2-cage in another way; namely, by insertion of three pyridyl moieties in the centre of each 'strap' [between the ether heteroatoms of **(4)**] to yield an extended cage of type **(5)** (Atkinson *et al.*, 1997). For this product molecular modelling indicated that the central cavity now approximated that of a 'slot', centred on the plane passing through the three pyridyl nitrogens (the calculations also confirmed that the *exo-exo* arrangement of the nitrogen caps remains strongly favoured).

The new cavity appeared ideal for insertion of flat aromatic-like rings. Indeed, consideration of its diameter as defined by the positions of the heterocyclic nitrogen atoms suggested that its dimensions were ideal for accepting a phloroglucinol guest which should be able to be suitably positioned to undergo hydrogen bonding, via its phenol hydrogens, to the trigonally orientated nitrogens. Accordingly, (**5**; R = *t*-Bu) was found to solubilise phloroglucinol in dichloromethane and chloroform. NMR evidence showed that it interacts in a 1:1 ratio with phloroglucinol, with the data in accord with this guest occupying the central cavity as postulated above. Molecular mechanics and semi-empirical molecular orbital (AM1) calculations also supported the reasonableness of such a host-guest structure. Further evidence for the role of hydrogen bonding in stabilising the above host-guest complex was obtained by repeating the experiment using the corresponding cage in which the pyridyl groups of **(5)** were replaced by three *m*-xylyl groups. In contrast to the previous case, there was no evidence for host-guest formation when this new cage was mixed with phloroglucinol.

Finally, NMR induced chemical shift data confirms that (**5**; R = *t*-Bu) interacts more strongly with phloroglucinol relative to a wide range of other mono-, bi- and triphenolic derivatives whose steric properties make them less than ideal for simultaneous binding to the trigonally disposed pyridyl nitrogens of **(5)**. Clearly, both the steric and electronic properties of **(5)** result in it being an ideal synthetic receptor for phloroglucinol.

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Early Cretaceous-Recent Landscape Evolution of the Copper Mine Range and Adjacent Areas Far West New South Wales

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Abstract. The Copper Mine Range, comprising Emsian-Eifelian (Devonian) strata of the Mulga Downs Group, lies 40 km west of the small settlement of White Cliffs in far west New South Wales, Australia. Its summit is an exhumed dissected surface, gently tilted southeast, which formerly lay beneath strata of the Early Cretaceous Rolling Downs Group. At three localities on the tilted surface there are small sarsen boulders of silcrete which are probably Oligocene in age. At the margin of the range there are a few localities where fluvial sandstones of the Eyre Formation, Paleocene- mid Eocene in age, unconformably overlie Devonian strata. More distant from the range silcrete, of Oligocene age, locally overlies strata of the Eyre Formation. These facts are consistent with the following geological history: (1) post-Early Cretaceous uplift/gentle folding followed by extensive erosion to form a landscape of plateaux and plains; (2) deposition of the Eyre Formation on the plains part of this landscape; (3) removal, by erosion, of much of the Eyre Formation during Late Eocene time and (4) Formation of silcrete caps (on the plains and the plateaux) during Oligocene time. Since Oligocene time there has been a further ~20 m of denudation of the plains part of the landscape whereas there has been only minor erosion of the plateaux.

Keywords: Landscape evolution, ?Mid Cretaceous folding, Eyre Formation, Cordillo Surface, denudation.

INTRODUCTION

Much of semi arid far west New South Wales is deeply weathered and it has little relief (Alipour *et al.*, 1996), and, in contrast to southeastern Australia, there have been few geomorphological studies in the area. However, in the Mootwingee district there are some plateaux such as the Copper Mine Range, which lie 150 m higher in elevation than the adjacent plains (Fig. la). They are characteristically developed on erosion-resistant Devonian sandstone. Ideas as to how the landscape in far west New South Wales evolved follow from observations made during investigation of the Emsian-Eifelian (Devonian) fluvial strata-forming the Copper Mine Range (Neef and Bottrill, 1996). The model developed here is partly like models developed by other

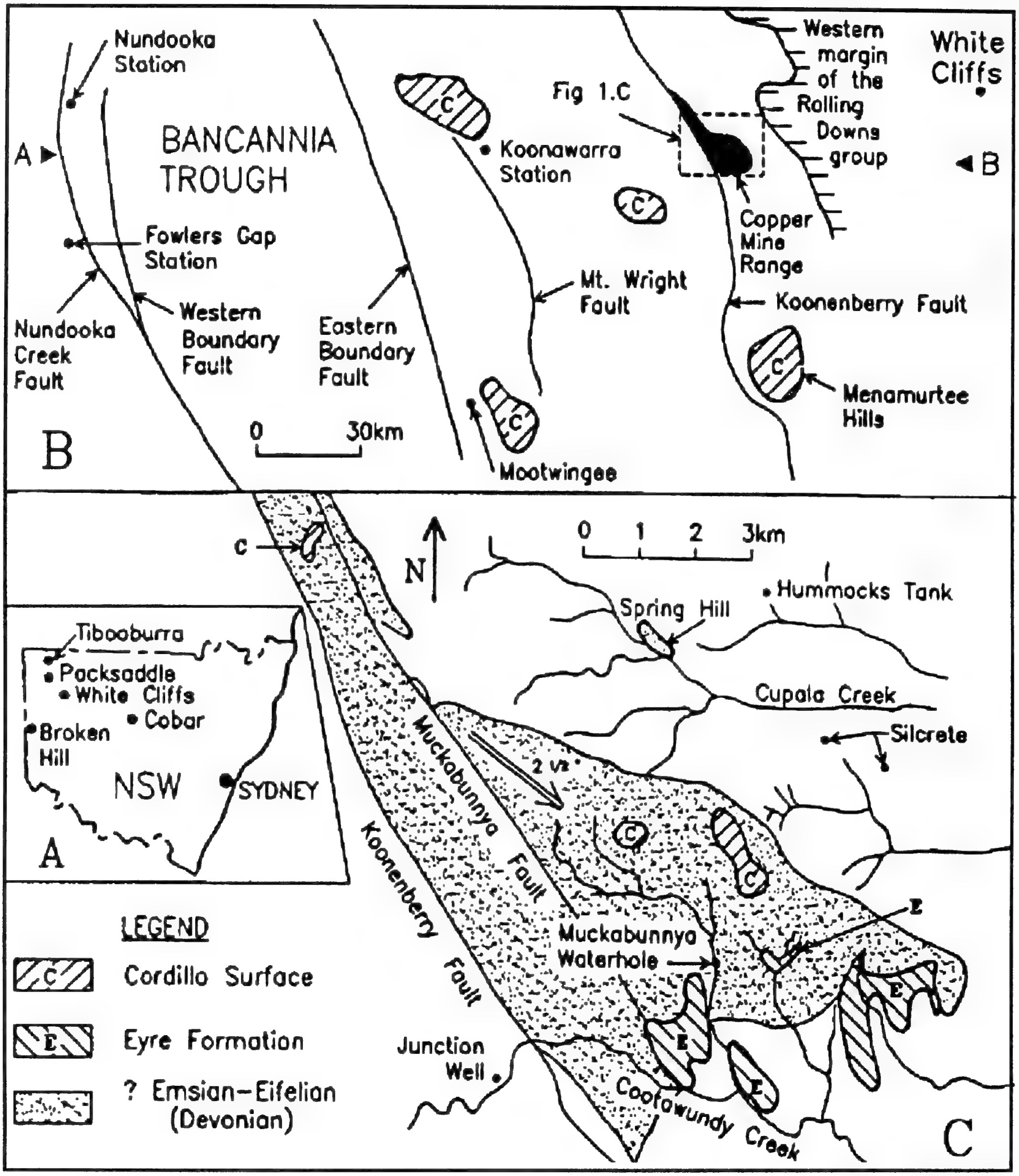

Fig. 1. **A.** Map showing the location of White Cliffs, Packsaddle and Tibooburra settlements in far west New South Wales, Australia.
B. Depicts the main faults of the White Cliffs-Nundooka Station district, plateaux with silcrete caps, the western margin of the Rolling Downs Group west of White Cliffs and the location of the Copper Mine Range.
C. Shows the distribution of Emsian-Eifelian strata in the southern part of the Copper Mine Range, and the location of the Eyre Formation and remnants of the Cordillo Surface. The direction of tilt of the plateau is shown by an arrow.

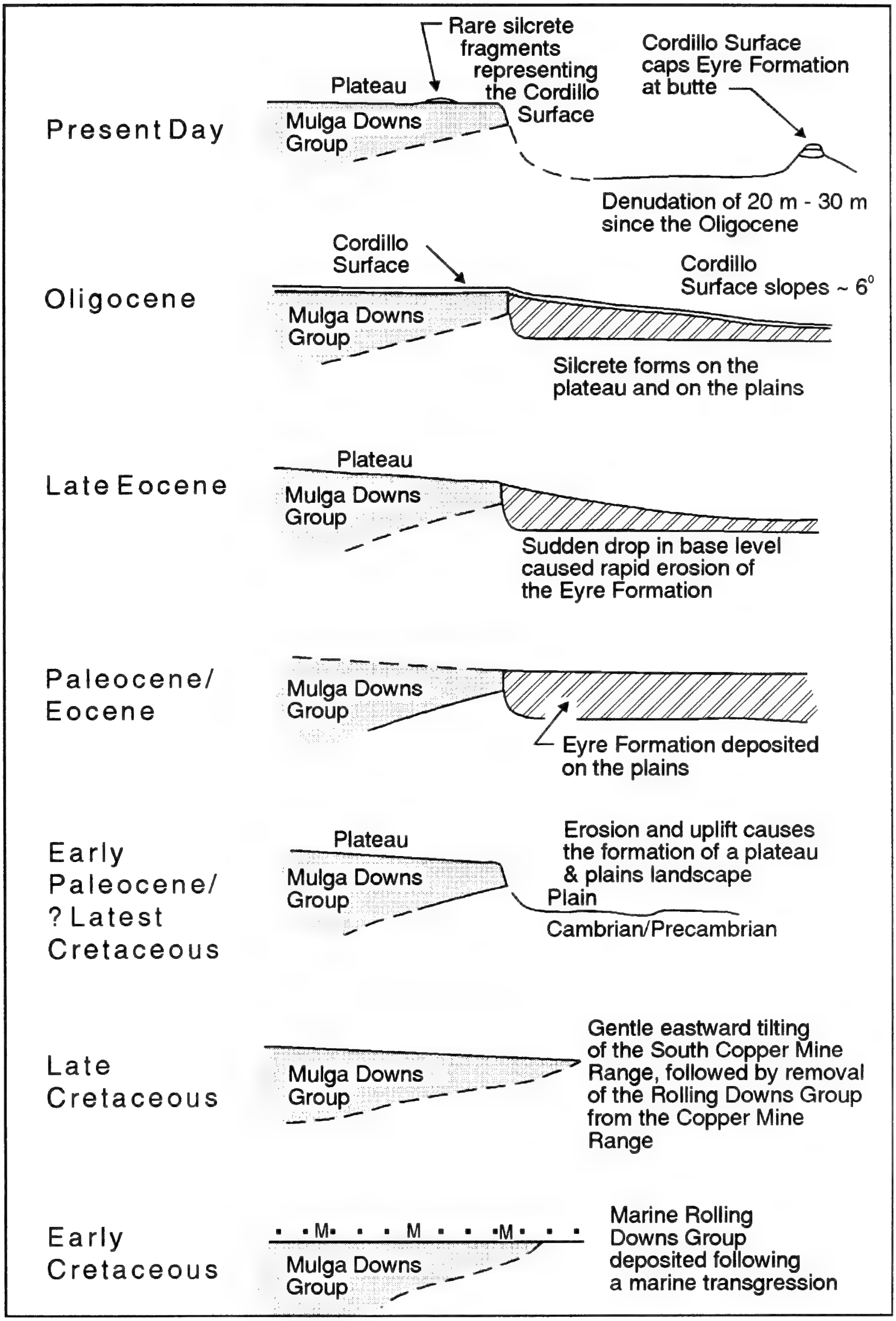

Fig. 2. Diagram shows the pre Aptian - present day history and landscape development near Cupala Creek in the Copper Mine Range.

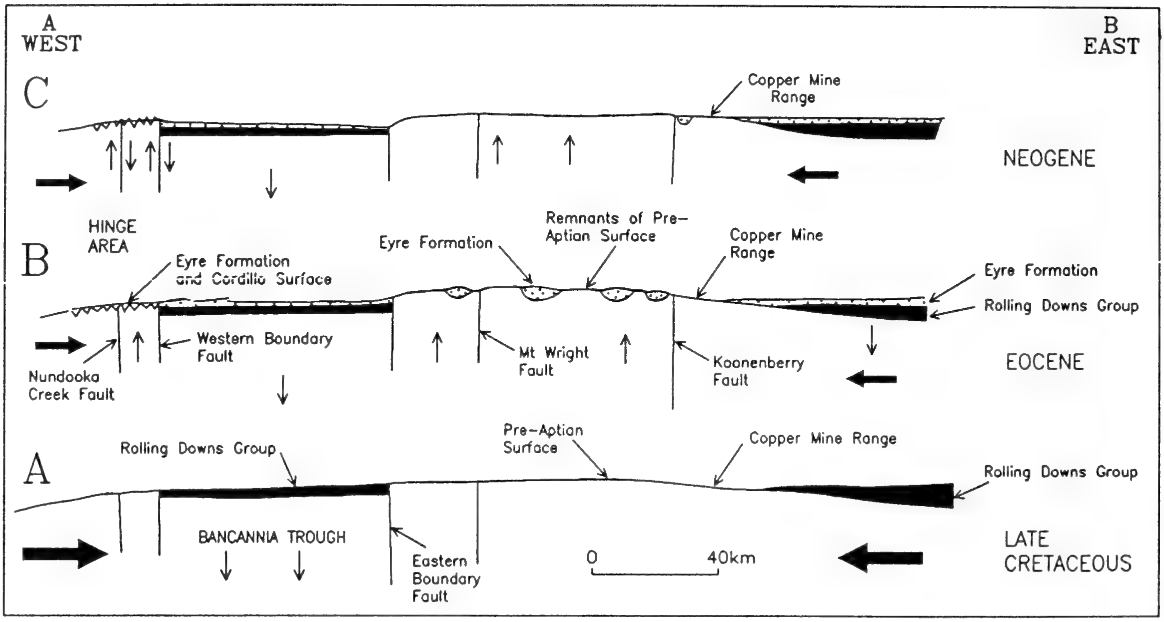

Fig. 3. East-West cross sections between White Cliffs and west of Nundooka Station show Late Jurassic - Neogene history of far western New South Wales. **A**. Late Cretaceous E-W compression caused gentle folding with an uplift culmination west of the Copper Mine Range and a downwarped area in the east near White Cliffs. **B**. Continuing E-W compression during Eocene time caused further uplift on the area between the Koonenberry and Eastern Boundary Faults. Eyre Formation is deposited on the plains part of the landscape. **C**. Cenozoic erosion has largely removed remnants of the Pre-Aptian surface and the Cordillo Surface between the Koonenberry and the Eastern Boundary Fault.

geomorphologists working elsewhere in inland Australia in that a part of the landscape has considerable antiquity and that Early Cretaceous exhumed surfaces are common (e.g. Twidale and Campbell, 1991).

REGIONAL AND LOCAL GEOLOGY AND PHYSIOGRAPHY OF THE COPPER MINE RANGE

Basement rocks of far-western New South Wales comprise Proterozoic strongly metamorphosed Willyama Series and mildly metamorphosed Wonaminta Series (Brunker *et al.*, 1971). Cambrian strata are thick and are mostly marine (Powell *et al.*, 1982) and there is also a huge thickness (~7 km) of Late Silurian-Early Carboniferous fluvial strata (Mt Daubeny Formation, Neef *et al.*, 1989; Mulga Downs Group, Evans, 1977). There are no Late Palaeozoic and early Mesozoic strata in the district but rocks of Jurassic age are known near Packsaddle (Brunker *et al.*, 1971) and near Tibooburra (Morton, 1982). In Early Cretaceous time, marine strata forming the Rolling Downs Group were deposited near White

Cliffs (Rose *et al.*, 1964); in the Bancannia Trough (Evans, 1977) and near Tibooburra (Rose *et al.*, 1967). Following a period of uplift during Late Cretaceous time (Veevers, 1984) the fluvial Paleocene-Mid Eocene Eyre Formation was deposited (Neef *et al.*, 1995).

The Copper Mine Range is triangular-shaped being 24 km long with a maximum width, in the south, of 8 km and narrower northwestwards (Fig. 1C). Its summit is a plateau which in the north and centre is ~150 m higher in elevation than the adjacent Pre-Cambrian and Palaeozoic strata. The plateau is commonly cliffed in the east and there are steep slopes towards the plain in the west. Gently folded Emsian-Eifelian (Devonian) sandstone underlies the plateau (Neef and Bottrill, 1996) whereas mudstone and a kimberlitic sill (Bottrill and Neef, 1998) have been much eroded to form valleys.

EARLY CRETACEOUS STRATA NEAR WHITE CLIFFS

Weathered fossiliferous marine claystone, the Rolling Downs Group, is known at White Cliffs (Rose *et al.*, 1964). It is largely Aptian in age although a bivalve, *Inoceramus* sp., found there is an Albian indicator (J. Morton, pers. comm., 1996), suggesting marine deposition occurred near White Cliffs throughout or in parts of, Aptian and Albian time (confirming previous studies of Frakes *et al.*, 1987). Twenty two kilometres WNW of White Cliffs fossil-rich (Devonian) boulders (erratics) crop out at Bunker Tank (Rose, 1974). They also indicate an Early Cretaceous age for the enclosing strata (Rose, 1974) and an original derivation from the Cobar area (Flint *et al.*, 1980). Southeast of Bunker Creek the 2.5°tilted plateau forming the Copper Mine Range (Fig. 1C) is overlain by Cretaceous strata at (Grid ref. 589 162, White Cliffs 1:250 000 Geological Map, Rose *et al.*, 1964, see also Fig. 1B). This indicates that the plateau represents an uplifted, gently tilted Early Cretaceous pre-Aptian exhumed surface.

West of Copper Mine Range the pre-Aptian surface is absent except within the Bancannia Trough where 61 m of Early Cretaceous strata are known (Baarda, 1968, Fig. 3). The surface is also present further west, near Lake Frome in South Australia, where it lies beneath the Cadna-Owie Formation (Callen and Coats, 1975) and at many other localities.

EYRE FORMATION

(Paleocene-mid Eocene, in age, Alley *et al.*, 1996)

About one kilometre south of Muckabunnya Waterhole, the fluvial formation, 15 m thick, comprises unfossiliferous, lightly indurated, pale-grey kaolinitic, very-fine sandstone, shale and minor fine gravel beds. However, the formation may have been ~40 m thick at the margin of the plateau (Fig. 2). Small remnants of the formation also crop out adjacent to stream beds 1.75 km ENE of the waterhole, indicating that the formation buried a hilly topography which is now being exhumed. Surprisingly, there is no evidence of sediment derivation from the adjacent lithified Devonian strata implying that burial of the Late Cretaceous topography was swift. Southeast of the Copper Mine Range geologic cross sections show almost complete erosion of the Rolling Downs Group and subsequent deposition of undifferentiated Cenozoic strata, considered here to be Eyre Formation and ~150 m thick (Frenda, 1965).

West of the Copper Mine Range near Nundooka Station the Eyre Formation also buries a Late Cretaceous landscape indicating substantial erosion there in Late Cretaceous time and the pre-Aptian surface is unrecognised there (Neef *et al.*, 1995).

SILCRETE OF THE CORDILLO SURFACE

Three periods of silcrete formation in Late Jurassic, Early Cenozoic, and Late Cenozoic time are known in northern South Australia (Wopfner, 1978). The Early Cenozoic (Oligocene) silcrete-capped surface (the Cordillo Surface) is most widespread in South Australia and far west New South Wales where it locally overlies Eyre Formation (at Fowlers Gap and Nundooka Stations, Fig. 1B) and is overlain by the Doonbara Formation, ?Miocene in age, at several localities (Neef *et al.*, 1995).

The plateau forming the Copper Mine Range is somewhat dissected by the headwaters of some streams but at three localities on the interfluves are small sarsen boulders of silcrete indicating that the range was previously capped by silcrete at least in part. Similar small sarsen boulders of silcrete are also known on the plateau surfaces at Menamurtee Hills (Wilson, 1967) and north of Koonawarra Station (Neef and Botrill *in prep.*; Fig. 2B). On the plains adjacent to the Copper Mine Range there are isolated buttes, ~100 m in diameter, which are capped by silcrete or ferricrete. A butte, which lies 3.5 km southeast of Spring Hill is capped by a 2 m thick nodular silcrete (which has rare impressions of leaves). The upper surface of the butte is declined to the NE at 6°, indicating that the silcrete on the buttes and the plateau are coeval (Fig. 2). (Had silcrete been present on the range during earliest Cretaceous time it is likely to have been removed during the Late Cretaceous erosion; hence an Oligocene age of silcrete formation is favoured).

DISCUSSION AND CONCLUSIONS

Shortly after the folding that initiated formation of the Eyre and White Cliffs Basins there was reactivation of the faults bounding the Bancannia Trough causing ~60 m of Early Cretaceous strata to be preserved there (Fig. 3) — perhaps during a short period of tensional stress (called a relaxation of regional uplift, Veevers, 1991). There followed substantial erosion of the uplifted gently folded pre-Aptian surface to form lowland areas whereas remnants of the pre-Aptian surface remain as plateaux (Figs. 2 & 3).

Subsequently, in the Paleocene, internal drainage, centred on what is now Lake Eyre, developed and much of the lowland parts of the landscape in western New South Wales (and the down warped areas of the Eromanga Basin) were sites of deposition (now represented by the EyreFormation). Palaeocurrent trends in Eyre Formation strata near Nundooka Station are consistent with northwest flow towards the Eyre Basin (Neef *et al.*, 1995, Fig. 11). However, since Paleocene time there was much greater subsidence in the Murray Basin than there was in the Eyre Basin (>610 m *vs* 210 m). (About 275 m of Murray Basin subsidence occurred during Eocene time; Veevers, 1991), which triggered its capture of the White Cliffs district drainage system (Veevers, 1984, Fig. 147H). Drainage capture rejuvenated streams and rivers of the West Darling causing the removal of ~40 m of Eyre Formation near Copper Mine Range. West of Tibooburra the base of the Eyre Formation dips westward at ~0.25° (Wopfner *et al.*, 1974, Fig. 10), indicating that folding along Mid Cretaceous trends continued into Cenozoic time, albeit at a gentler rate (Fig. 3).

The location of the sarsen boulders of silcrete on the Copper Mine Range and the location of the silcrete caps on the plain indicate the location of the early Oligocene landscape and the amount of late Eocene erosion that occurred, and also show that there has been little post Oligocene erosion of the sandstone parts of the plateaux (Fig. 3). (Similar low rates of erosion of sandstone are known in cratonic parts of northern Australia; Nott, 1994). However, areas underlain by shale and the ultrabasic sill are deeply eroded. Some of this erosion must have occurred during Late Cretaceous time, however. The plains part of the landscape are commonly 20 m - 30 m lower in elevation than they were in Oligocene time indicating an average denudation rate there of 1 m -1.5 m/10^6 yrs.

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Unnamed Palladium Telluride Minerals from Broken Hill, New South Wales

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Abstract. Two groups of unnamed palladium tellurides are present in several deposits near Broken Hill, New South Wales. The first corresponds to bismuthian Pd_8Te_3. A mercurian analogue has also been found at Mulga Springs. The second corresponds to bismuthian $Pd_{20}Te_7$. Both phases are known synthetically, but have not yet been described as valid species. Their relation to similar phases is discussed and the appropriate portion of the Pd-Te-Bi phase diagram reinterpreted in the light of naturally occurring species and recent synthetic studies.

INTRODUCTION

Small, but very rich (up to 100 ppm Pt and Pd) platinum group element (PGE) deposits have been known in the Broken Hill district of New South Wales, Australia, for more than a century (Jaquet, 1893, 1894; Mingaye, 1889, 1892). PGE are associated with a belt of altered and folded meta-peridotites which intrude the Thorndale Gneiss sequence of the Broken Hill Block (Barnes, 1988; Stevens, 1980); they occur with base metal mineralization (pyrite, chalcopyrite, pyrrhotine, pentlandite, violarite) at the contacts of the meta-peridotite, but more commonly in remobilised sulfides in shear zones, sometimes at the contact and sometimes at some distance from it (Elvy *et al*., 1998).

Early analyses of concentrates from Mulga Springs and Little Darling Creek (Fig. 1) revealed the presence of Pt, Ir, Os, Pb, Zn, Sb, As, Au, Ag and Bi, and it was considered likely that sperrylite, $PtAs_2$, was present in the ore samples, but in too finely divided a state to be concentrated by conventional gravity methods of the time (Mingaye, 1892). Until recently, no report of PGM in these deposits has been made. Here, we report in detail the widespread occurrence of unnamed palladium telluride minerals in gossans at Mulga Springs, Lit-

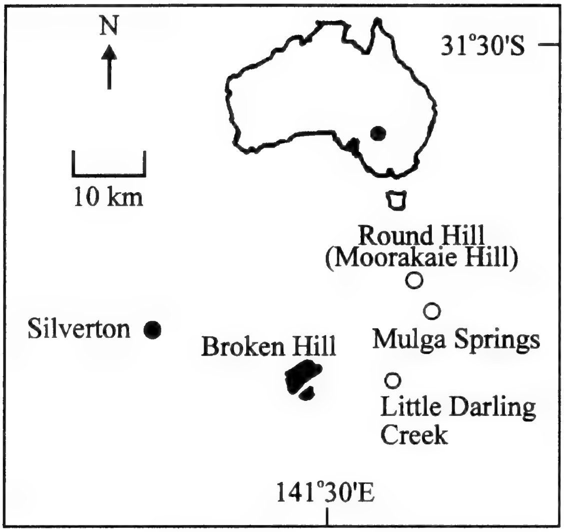

Figure 1. Locations of the three deposits near Broken Hill, New South Wales.

tle Darling Creek and Moorkaie (Round) Hill. A list of other species identified in the deposits, including platinum and separate palladium minerals, has been reported elsewhere (Elvy *et al.*, 1998).

EXPERIMENTAL

Samples of gossan after sulfides were collected from a small costean next to the entrance of a shallow dipping adit at Mulga Springs and in the roof of the adit, from the upper of two prospecting pits on the south flank of Mookaie Hill and from the roof of the adit in the Little Darling Creek workings. A second suite of samples was taken at the latter site from an ore dump adjacent to a prospecting pit near Little Darling Creek (sample LDC9).

Heavy concentrates of samples crushed to minus 80 mesh were prepared using a Haultain superpanner. Head and middle fractions were embedded in epoxy and a flat surface ground for microprobe examination. The samples were examined optically, then coated with carbon for microprobe analysis using a Cameca Camebax microprobe equipped with four vertical wavelength-dispersive spectrometers analysing from B to U. The instrument was also equipped with an EDS spectrometer analysing from Na to U, used for qualitative identification of mineral species. All WDS spectrometers were calibrated against known mineral and elemental standards. Proton induced X-ray emission (PIXE) analyses were carried out using the CSIRO heavy ion analytical facility at North Ryde.

UNNAMED PALLADIUM TELLURIDES

The most common palladium tellurides from the Broken Hill district correspond to the ideal end-member compositions $Pd_{20}Te_7$ and Pd_8Te_3. However, significant amounts of Bi substitute in both series save for one specimen; in this case, Hg substitutes for Te in Pd_8Te_3. There has been a number of reports of compound formation in the Pd-Te-Bi ternary system. The most extensive of these, especially at high mol fractions of Pd, is the report of El-Boragy and Shubert (1971), based on binary Pd-Te phases Pd_4Te, Pd_3Te, Pd_3Te_2 and Pd_2Te, and binary Pd-Bi phases $PdBi_3$ and Pd_5Bi_3. However, a more recent and thorough study of phase relations in the Pd-Te system has shown that the phases that do exist in this binary are $Pd_{17}Te_4$, $Pd_{20}Te_7$, Pd_8Te_3, Pd_7Te_3, Pd_9Te_4, Pd_3Te_2, PdTe and $PdTe_2$ (Kim *et al.*, 1990). Of these, Pd_9Te_4, PdTe and $PdTe_2$ are the minerals telluropalladinite, kotulskite and merenskyite, respectively. None of these has been observed in the Broken Hill deposits, although froodite, $PdBi_2$, and native bismuth have been found with some of the unnamed Pd-Te-Bi minerals (Elvy *et al.*,

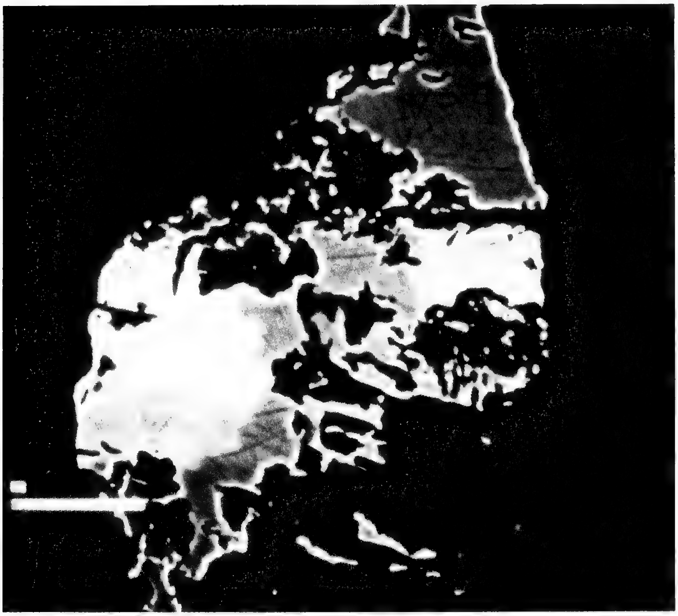

Figure 2. Weathered grain of $Pd_8(Te,Bi)_3$ from Little Darling Creek. Scale bar is 10 micrometres in length.

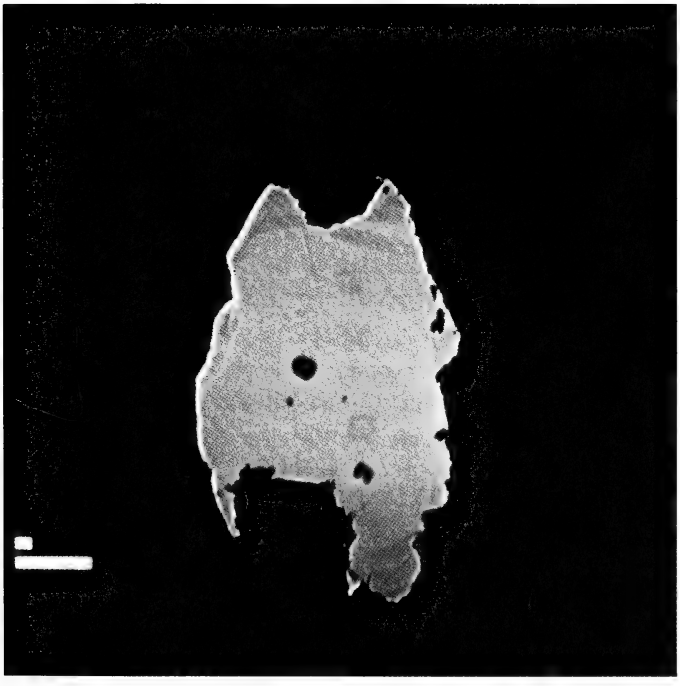

Figure 3. Strongly embayed grain of $Pd_8(Te,Hg)_3$ from Mulga Springs. Scale bar is 10 micrometres in length.

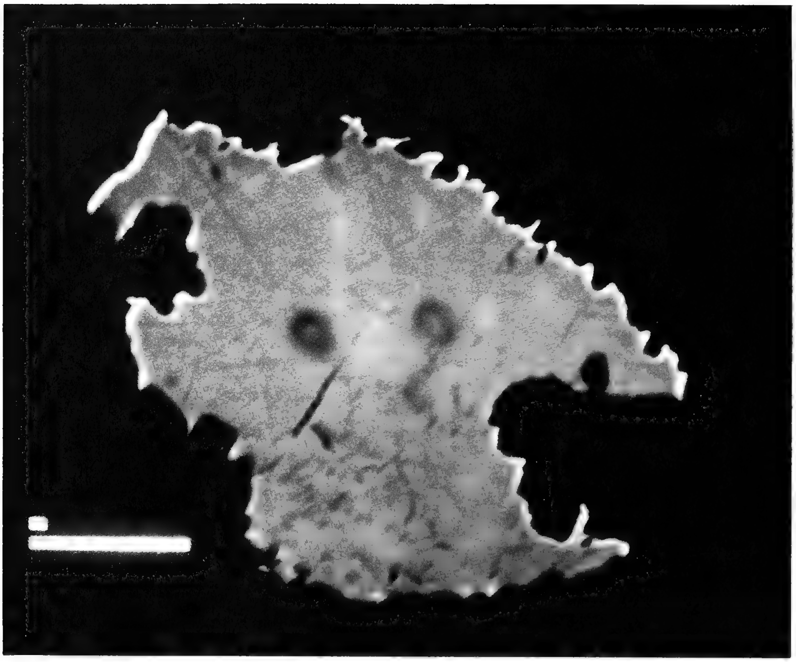

Figure 4. Weathered grain of $Pd_{20}(Te,Bi)_7$ grain from Little Darling Creek. Scale bar is 10 micrometres in length. Circular areas in centre of grain are due to the microprobe beam.

1998).

Analyses of phases from Broken Hill based on Pd_8Te_3 stoichiometries are listed in Table 1, with totals based on Pd + Pt = 8; Pt is a very minor substituent. Reasonably good analytical totals and sums for Te + Bi + As + Sb (the latter two being present in minor amounts) were obtained for samples which had very pitted surfaces. Apart from sample 11, the only significant substitution in these phases is by Bi for Te, up to Te:Bi *ca* 1.4:1. Grains up to 80 μm across have been observed but they are strongly embayed as a result of weathering (Fig. 2). In some samples of gossan prepared as polished blocks, no Pd minerals were observed at all (although sperrylite and native platinum were); PIXE analyses, however, showed significant Pd in goethite, this indicating complete decomposition of the primary Pd minerals.

Cabri (1981) first reported an unnamed palladium telluride of composition Pd_8Te_3, with minor Pt and Hg and Sb not detected, from the Stillwater Complex, Montana. It was associated with (*inter alia*) keithconnite, $Pd_{20}Te_7$ (*vide infra*). Likewise, Grokhov-skaya *et al.* (1992) reported an unnamed $(Pd, Pt, Ag)_8$ $(Te, Bi)_3$ from the Lukkulaisvaara Pluton, Russia, but analyses were of lower quality [$(Pd_{7.58}Pt_{0.06}Ag_{0.36})_{\Sigma 8.00}(Te_{2.76}Bi_{0.10})_{\Sigma 2.86}$, $(Pd_{7.43}Pt_{0.04}Ag_{0.53})_{\Sigma 8.00}Te_{3.30}$ and $(Pd_{7.87}Pt_{0.01}Ag_{0.13})_{\Sigma 8.00}(Te_{1.70}Bi_{1.66})_{\Sigma 3.33}$; Te:Bi up to ~1:1]. Material from Broken Hill displays the same optical properties as those reported by Cabri (1981). Percentage reflectivities at 546 and 589nm are 51.2 and 53.8, respectively. Unfortunately, we have not yet been able to recover a grain large enough to record X-ray data using Gandolfi techniques.

One grain was recovered in the Mulga Springs concentrate which corresponds to $Pd_8(Te,Hg)_3$ with Te:Hg *ca* 3.2:1, and with minor Bi. No other elements were detected in this highly embayed, corroded grain (Fig. 3). Temagamite, Pd_3Te_3Hg, is the only

TABLE 1. Analyses of grains with Pd_8Te_3 stoichiometries (wt %)[a].

Sample No.[b]	Pd	Pt	Te	Bi	Hg	As	Sb	Rem	Total
1	64.51	0.35	20.41	13.35					98.62
2	64.44	0.41	20.02	13.89					99.14
3	64.68		18.87	16.14					100.30
	63.53		19.23	14.33					97.20
	63.53		19.41	14.49					97.74
4	68.58	1.53	25.57	8.23				0.18[c]	104.09
5	71.82		27.3	4.99		0.85		0.36[d]	105.33
6	71.14	0.13	29.46	2.49		0.59		0.39[e]	104.20
7	70.82	tr[f]	29.52	1.63		0.52		0.34[f]	102.83
8	66.41		16.62	19.85		0.30		0.37[g]	103.55
9	66.80		17.41	19.77		0.64		0.34[h]	104.96
10	67.10		16.92	18.73		0.42	0.51	0.40[i]	104.08
11	63.92		22.14	1.01		10.39			97.57
	64.65		22.18	0.88		10.22			97.99
	64.35		21.83	0.86		10.65			97.67

[a] Values missing for particular elements indicates that they were not detected at the 0.01 wt% level; Rem = remainder.

[b] **1:** Mulga Springs (costean) $(Pd_{7.98}Pt_{0.02})_{\Sigma 8.00}(Te_{2.11}Bi_{0.84})_{\Sigma 2.95}$;
2: Mulga Springs (costean) $(Pd_{7.97}Pt_{0.03})_{8.00}(Te_{2.07}Bi_{0.88})_{2.95}$;
3: Mulga Springs (costean; three analyses); $Pd_8(Te_{1.95}Bi_{1.02})_{\Sigma 2.97}$; $Pd_8(Te_{2.02}Bi_{0.92})_{\Sigma 2.95}$; $Pd_8(Te_{2.04}Bi_{0.93})_{\Sigma 2.97}$;
4: Little Darling Creek (LDC9); $(Pd_{7.90}Pt_{0.10})_{\Sigma 8.00}(Te_{2.46}Bi_{0.48})_{\Sigma 2.94}$;
5-10: Upper pit, Moorkaie Hill; analyses give, respectively, $Pd_{8.00}(Te_{2.54}Bi_{0.28}As_{0.13})_{\Sigma 2.95}$, $(Pd_{7.92}Pt_{0.08})_{\Sigma 8.00}(Te_{2.73}Bi_{0.14}As_{0.09})_{\Sigma 2.96}$, $Pd_{8.00}(Te_{2.78}Bi_{0.09}As_{0.08})_{\Sigma 2.95}$, $Pd_{8.00}(Te_{1.67}Bi_{1.22}As_{0.05})_{\Sigma 2.94}$, $Pd_{8.00}(Te_{1.74}Bi_{1.21}As_{0.11})_{\Sigma 3.06}$, $Pd_{8.00}(Te_{1.68}Bi_{1.14}As_{0.07}Sb_{0.05})_{\Sigma 2.94}$;
11: Mulga Springs (costean); three analyses give $Pd_{8.00}(Te_{2.30}Hg_{0.69}Bi_{0.06})_{3.05}$, $Pd_{8.00}(Te_{2.29}Hg_{0.67}Bi_{0.06})_{3.02}$, $Pd_{8.00}(Te_{2.26}Hg_{0.70}Bi_{0.05})_{3.01}$, respectively;[c] Sum of traces of Fe, Ni, Cu, Os, Ir, As (0.01%), Sn; [d] Sum of traces of Fe, Cu, Ir, S, Sn; [e] Sum of traces of Os, Ir, S; [f] Sum of traces of Os, Ir, Pt (0.04%), S; [g] Sum of traces of Fe, Os, Ir, S, Sb (0.09%), Sn; [h] Sum of traces of Fe, Cu, Os, Ir, S, Sn; [i] Sum of traces of Fe, Os, Ir, S, Sn.

named Pd-Te-Hg mineral. It is clearly not this phase and three analysEs of the only grain discovered give consistent results with the formula for mercurian Pd_8Te_3. Optical properties are virtually identical to those of the bismuthian analogues with percentage reflectivities at 546 and 589 nm being 52.7 and 54.8, respectively. The grain was too small to recover to record X-ray data.

Another group of analyses of grains from both sites at Little Darling Creek and Mulga Springs correspond with composition $Pd_{20}(Te,Bi)_7$, as reported in Table 2. Minor Pt, Fe, Cu and Os substitute in some of the grains analysed; traces of arsenic and antimony are detected in certain of them. Reasonable totals were recorded for these very weathered grains (Fig. 4) and calculations for Pd + Pt + Fe + Cu + Os = 20 give good sums for Te + Bi + As + Sb (Table 2). The Te:Bi ratio is greater than *ca* 3:1. No grain recovered so far is large enough to permit an X-ray examination.

In reflected light, the grains are pale cream and possess properties in accord with those described by Kim *et al.* (1990) for synthetic $Pd_{20}Te_7$, whose structure is known (Wopersnow and Schubert, 1977). Berlincourt *et al.* (1981) have suggested that the ideal formula for keithconnite is $Pd_{20}Te_7$. However, while this was considered in the original description of the mineral (Cabri *et al.*, 1979), it was noted that the X-ray powder diffraction patterns were different, even though the unit cells were similar and the space group, $R\bar{3}$, is the same for keithconnite and $Pd_{20}Te_7$. Furthermore, analyses of keithconnite are somewhat Pd-deficient and Cabri *et al.* (1979) noted that they were unable to synthesise the mineral. It is possible that keithconnite is in fact another species and that the grains from Broken Hill,analysed here, correspond to bismuth-substituted, synthetic $Pd_{20}Te_7$. We are engaged in a search for larger grains of the palladium tellurides in order to fully characterise them as minerals. We have, however, synthesised an alloy of composition $Pd_{20}Te_{5.25}Bi_{1.75}$ by melting the constituent element together and cooling from 480°C at 0.1°C min^{-1}. The product had a powder X-ray pattern corresponding to synthetic $Pd_{20}Te_7$ (Wopersnow and Schubert, 1977). A fragment was cut and polished. Under reflected light it was cream in colour and consisted, as far as could be ascertained, of a single phase.

In the light of the compositions of the phases that we have identified from Broken Hill, and since the nature of the phases present in the Pt-Te system has been more precisely established (Kim *et al.*, 1990), it is of interest to re-examine the Pd-Te-Bi ternary phase diagram of El-Boragy and Schubert (1971). A section of the appropriate ternary diagram is shown in Figure 5. Originally the diagram was plotted for a temperature of 480°C. We have reinterpreted it by correcting the stoichiometries proposed originally, identifying phases which had been attributed in error, and by adding the data accumulated in Tables 1 and 2. For this latter purpose we have plotted our data in terms of total "cations" (Pd + Pt, *etc.*) for Pd and Bi and Te contents (filled circles). For the mercury containing phase the data on the figure are plotted in terms of Pd and (Te + Hg) being Te alone.

In Figure 5, the limit of solid solution for bismuthian tellurian palladium reported by El-Boragy and Schubert (1971) is maintained. Similarly, their interpretation of the existence of the species Pd_3Bi and Pd_5Bi_3 is adopted. However, Pd-Te species are attributed to the recent studies of Kim *et al.* (1970). Thus the W, X, Y and Z phases of El-Boragy and Schubert (1971) are attributed to the compounds Pd_5Sb_2 (in structural terms) Pd_7Te_3, Pd_8Te_3 and $Pd_{20}Te_7$, respectively. Analyses of species from the Broken

TABLE 2. Analyses of grains with $Pd_{20}Te_7$ stoichiometries (wt %)[a].

Sample No.[b]	Pd	Pt	Fe	Cu	Os	Te	Bi	As	Sb	Rem	Total
1	69.33		0.44	tr[c]	tr[c]	25.08	8.33	0.06		0.17[c]	103.41
2	68.41	0.06	0.47		0.24	24.39	8.64	0.04		0.10[d]	102.35
3	65.35	0.31	0.51	0.10	0.14	23.21	7.54	tr[e]		0.15[e]	97.31
4	67.32	0.44	0.57	0.06	0.08	23.77	7.54	0.11		0.05[f]	99.96
5	66.22	0.20	0.60	0.06	0.19	23.99	7.73			0.13[g]	99.12
6	68.90	0.13	0.18	tr[g]		21.11	11.54	0.22	1.21	0.30[h]	103.59
7	65.57	0.21	0.47			23.79	8.13			0.17[i]	98.34
8	68.46	1.64	0.27	0.18	tr[i]	24.83	8.88			0.24[j]	104.50
9	69.80	1.15	0.46	0.12	0.09	25.64	8.28			0.11[k]	105.65
10	66.70	5.31				25.83	6.41	0.05		0.06[l]	104.36
11	63.11			0.97	0.67	18.65	13.97				97.40

[a] Values missing for particular elements indicates that they were not detected at the 0.01% level; Rem = remainder.

[b] **1-7**: Little Darling Creek (adit); analyses correspond, respectively, to $(Pd_{19.76}Fe_{0.24})_{20.00}$-$(Te_{5.96}Bi_{1.21}As_{0.02})_{\Sigma7.19}$, $(Pd_{19.69}Pt_{0.01}Fe_{0.26}Os_{0.04})_{\Sigma20.00}(Te_{5.85}Bi_{1.27}As_{0.02})_{7.14}$, $(Pd_{19.59}Pt_{0.05}Fe_{0.29}Cu_{0.05}Os_{0.02})_{\Sigma20.00}$-$(Te_{5.80}Bi_{1.15})_{\Sigma6.95}$, $(Pd_{19.57}Pt_{0.07}Fe_{0.32}Cu_{0.03}Os_{0.01})_{\Sigma20.00}(Te_{5.76}Bi_{1.12}As_{0.05})_{\Sigma6.93}$, $Pd_{19.57}Pt_{0.03}Fe_{0.34}Cu_{0.03}Os_{0.03})_{20.00}$-$(Te_{5.91}Bi_{1.16})_{\Sigma7.08}$, $(Pd_{19.88}Pt_{0.02}Fe_{0.10})_{\Sigma20.00}(Te_{5.08}Bi_{1.70}As_{0.09})_{\Sigma6.87}$, $(Pd_{19.69}Pt_{0.04}Fe_{0.27})_{\Sigma20.00}(Te_{5.96}Bi_{1.24})_{\Sigma7.20}$;
8-9: Little Darling Creek (LDC9); analyses correspond, respectively, to $(Pd_{19.52}Pt_{0.25}Fe_{0.15}Cu_{0.08})_{\Sigma20.00}$(-$(Te_{5.90}Bi_{1.29})_{\Sigma7.19}$ and $(Pd_{19.52}Pt_{0.18}Fe_{0.24}Cu_{0.05}Os_{0.01})_{\Sigma20.00}(Te_{5.98}Bi_{1.18})_{\Sigma7.16}$;
10: Mulga Springs (adit); As not included in calculation of formula; $(Pd_{19.17}Pt_{0.83})_{\Sigma20.00}$ $(Te_{6.19}Bi_{0.94})_{\Sigma7.13}$;
11: Mulga Springs (costean); $(Pd_{19.38}Cu_{0.50}Os_{0.12})_{\Sigma20.00}(Te_{4.78}Bi_{2.18})_{\Sigma6.96}$; [c] Sum of traces of Ni, Cu(0.01%), S, Sn, Os (0.03%); [d] Sum of traces of Ni, S, Sn; [e] Sum of traces of Ni, As (0.01%), S, Sn; [f] Sum of traces of S, Sn; [g] Sum of traces of Ni, Ir, Rh, S, Sn; [h] Sum of traces of Cu (0.01%), Os, Ir, S, Sn; [i] Sum of traces of Cu (0.01%), Ir, S, Sn; [j] Sum of traces of Ni, Os (0.02%), Ir, S, Sn; [k] Sum of traces of Ni, Ir, Sn; [l] Sum of traces of Fe (0.04%), Ni.

Hill deposits extend the ranges of the appropriate phases, as shown in Figure 5.

Further investigations will be required in order to establish the limits of stability of these compounds. In particular, further work would seem to be required on the Bi-rich phases. El-Boragy and Schubert (1971) found a miscibility gap between Pd_3Bi and "Pd_3Te" which would be explained by the true stoichiometry of the latter. Details of other binary phases in the Pd-Bi system remain enigmatic not only with respect to

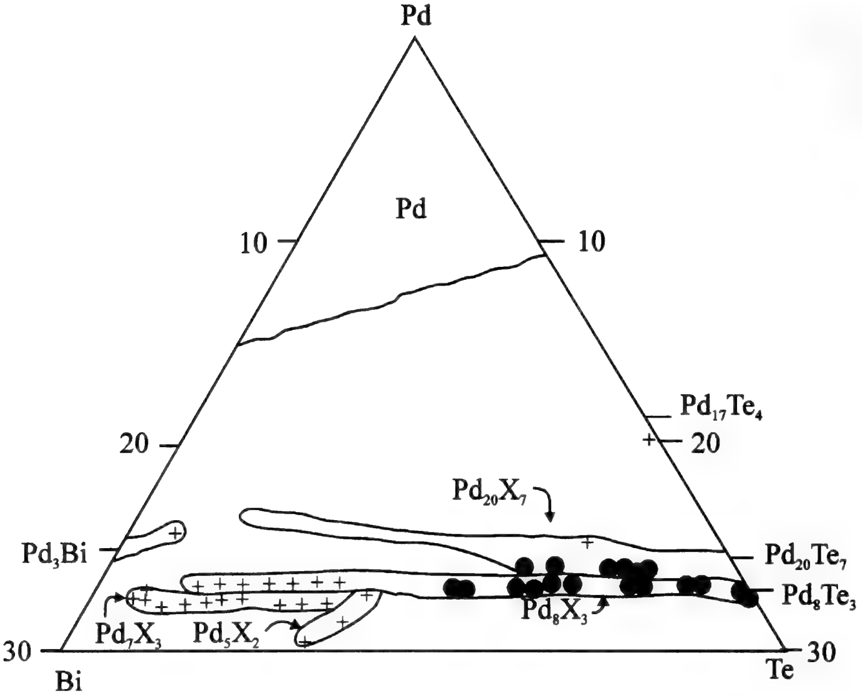

Figure 5. Revised phase diagram for the Pd-rich section of the Pd-Ti-Bi system at *ca* 500°C. Data of El-Boragy and Schubert (1971) are shown as crosses (for cases when a single phase alone is present). Closed symbols refer to phases recovered from the Broken Hill localities (see text). The extended field of phases related to $Pd_{20}Te_7$ (bismuth-rich) is plotted as by El-Boragy and Shubert based on samples which contained more than one phase.

this ternary system, but also in the light of other congeners involving Sb and As (Weiser and Barth, 1996).

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The Broken Hill Meteorite, New South Wales, Australia

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(Communicated by D.F. Branagan)

Abstract. The Broken Hill meteorite is a newly described L5 chondrite found in 1994 near the town of Broken Hill, in western New South Wales, Australia. It is a single stone, of mass 34 kg when found, and with a thin surface film of iron hydroxide and calcrete. The meteorite contains abundant chondrules, mainly of olivine-orthopyroxene in a coherent matrix of olivine, orthopyroxene and oligoclase. Troilite is the main opaque mineral, with only minor amounts of taenite and kamacite, and rare chromite. Electron probe microanalysis of the main minerals gave compositions typical of L5 chondrites. The Broken Hill meteorite shows no evidence of shock features and is moderately low on the scale of weathering. It is considered to be a distinct find, unrelated to similar meteorites found in the region.

INTRODUCTION

The Broken Hill meteorite was found in December 1994 on a surface of blown sand about 20 km NE of Broken Hill, New South Wales, Australia (approximately 31°50'S; 141°46'E) (Fig. 1). The meteorite was purchased from the finder by a group of mineral and meteorite dealers, who proceeded to slice the meteorite and distribute portions to various institutions and individuals. The main mass (Figs 2a,b), which measures 25 x 18 (the cut face) x 13 cm and has a mass of 11.9 kg, remains in the possession of the dealers. Several pieces (286 g, 49 g and 23 g) were obtained by the Museum of Victoria and this study has been based on the 49-gram type specimen, which is registered E14312. The name and the data for classification were approved by the Nomenclature Committee of the Meteoritical Society early in 1996.

Figure 1: Locality map

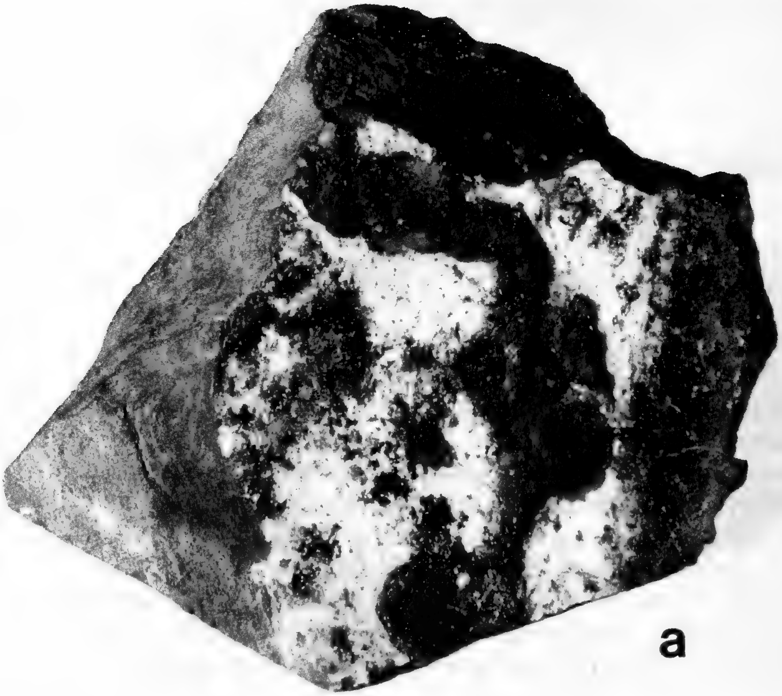

Figure 2a. Remaining piece of the Broken Hill meteorite showing partial surface coating of calcrete (white).

DESCRIPTION

Before cutting, the meteorite was a large irregular block, with dimensions 40 x 26 x 20 cm, and a mass of about 34 kg. There is no distinctive fusion crust, rather the surface is a dark brown coating, less than 0.5 mm thick, of iron hydroxide, some of which has been spalled off, possibly by wind ablation. Parts of the surface support a thin film of white calcrete.

The meteorite contains abundant, distinct to poorly defined chondrules (about 40 volume %). They are enclosed in a recrystallised, heavily iron-stained, but coherent matrix of irregular fragments of olivine and orthopyroxene, together with fragmented chondrules and small grains and interstitial areas of oligoclase. The complete chondrules are mostly between 1 and 3 mm in diameter, with a few reaching 5 mm. They show a wide variety of textures, but most are either barred, porphyritic or granular types, involving olivine and/or orthopyroxene. There are a few chondrules showing fine-scale barring of olivine/oligoclase and diopside/oligoclase. Chondrules consisting of single crystals of olivine are rare. Opaque minerals make up less than about 5 volume % of the meteorite. The most abundant opaque mineral is troilite, which is often altered to goethite.

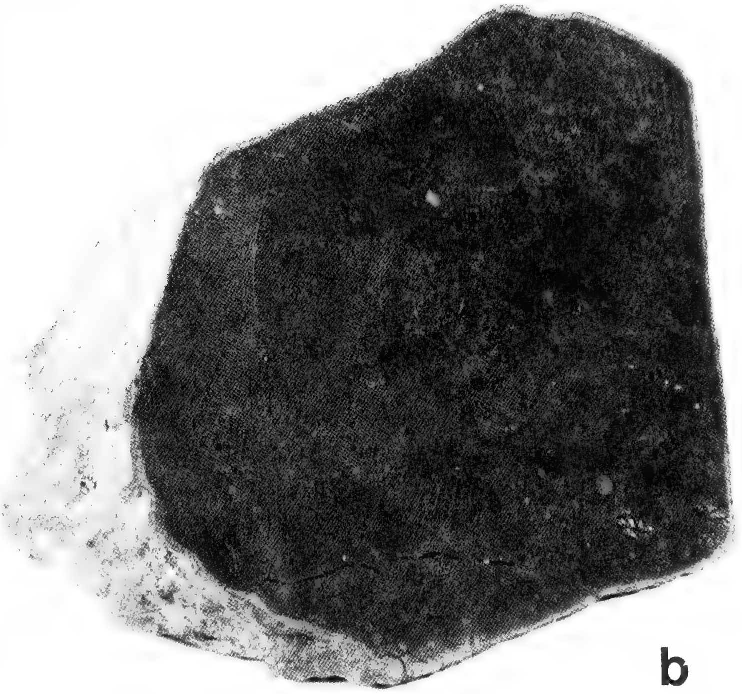

Figure 2b. Remaining piece of the Broken Hill meteorite showing cut face 25 cm wide.

Coarser patches of troilite up to 5 or 6 mm across have weathered to form cavities in which gypsum has crystallised. Small distinct grains of kamacite and taenite are present but are not conspicuous. Chromite occurs rarely as very small inclusions in olivine grains.

Microprobe analyses were obtained on all the main phases using a Cameca SX50 instrument operating at 15 kV and a 25 μA beam current, and using both natural and synthetic standards. The olivine in both chondrules and matrix is homogeneous, with an average composition expressed as $Fo_{73.9}Fa_{25.6}Te_{0.5}$ (molecular %), i.e., 100(Fe+Mn)/(Fe+Mn+Mg) = 26. The low-Ca orthopyroxene is Mg-rich ('bronzite') with an average composition shown by the formula $En_{76.4}Fs_{22.0}Wo_{1.5}$, and the clinopyroxene in barred chondrules is diopside ($En_{46.6}Wo_{45.0}Fs_{8.5}$). The oligoclase in the matrix and barred chondrules has an average composition $Ab_{84}An_{11}Or_{6}$. Only 5 analyses of the taenite and kamacite grains were obtained; these show compositional ranges represented by Fe/Ni = 2.3-2.4 and 15-19 (weight % basis) respectively. The chromite contains small amounts of Al, Ti, Mg and V (see Table 1).

CLASSIFICATION

A full chemical analysis of the Broken Hill meteorite was not undertaken, but the meteorite can be classified on mineralogical and textural grounds. Based on the above features, and according to the chondrite classification criteria of Dodd (1981) and Van Schmus & Wood (1967), the Broken Hill meteorite is a borderline L5-6 chondrite. However the wollastonite content of the orthopyroxene is within the range of values typically shown by orthopyroxene from L5 chondrites (Scott *et al.*, 1986). The absence of undulose extinction and planar fractures in olivine indicates that the meteorite is unshocked (S1 on the scale of Stöffler *et al.*, 1991). The weathering grade is estimated to be W2 (Wlotzka, 1993), suggesting the meteorite fell between 5000 and 15 000 years ago.

DISCUSSION

There are several other records of similar meteorite finds in the general region, specifically the Cockburn and Silverton meteorites. An L6 meteorite was found in 1946, at a locality about 9 km SE of Cockburn, South Australia (32°8'S, 141°4'E) and about 70 km SW of the discovery site of the Broken Hill meteorite. From the description by Johnson and McColl (1967), the Cockburn meteorite has a similar weathering crust to the Broken Hill meteorite, but contains nickel-iron grains in the form of 'plessite'. The Silverton meteorite was probably found in about 1883, but not noticed until 1933 when it was rediscovered in a museum collection in South Australia. The exact recovery site is not documented, but the town of Silverton (31°53'S, 141°12'E) is about 40 km west of the Broken Hill meteorite find. From the description by Spencer (1934), the Silverton meteorite has a well-developed fusion crust, and contains considerably fewer chondrules and higher contents of opaque minerals than the Broken Hill stone. It therefore appears that the Broken Hill meteorite is a distinct, previously unrecorded find.

ACKNOWLEDGEMENTS

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TABLE 1. Representative electron microprobe analyses of non-metallic minerals in the Broken Hill meteorite

	1	2	3	4	5
SiO_2	38.18	55.20	53.81	64.95	-
TiO_2	0.01	0.14	0.53	0.09	1.86
Al_2O_3	0.02	0.17	0.56	20.09	6.64
Fe_2O_3	-	-	-	0.51	34.57
Cr_2O_3	0.01	0.12	0.88	-	54.15
NiO	0.04	0.02	0.07	-	0.13
FeO	23.30	14.43	5.27	-	-
MnO	0.46	0.47	0.18	-	0.63
MgO	37.58	28.08	15.97	-	1.81
CaO	0.02	0.86	21.52	2.35	0.03
Na_2O	-	0.02	0.53	9.68	-
K_2O	-	-	-	0.85	-
Total	99.62	99.71	99.32	99.32	99.83

1. Olivine (average in chondrules and matrix) $Fo_{73.9}Fa_{25.6}Te_{0.5}$
2. Orthopyroxene (average in chondrules and matrix) $En_{76.4}Fs_{22.0}Wo_{1.5}$
3. Clinopyroxene (in barred chondrule) $En_{46.6}Wo_{45.0}Fs_{8.5}$
4. Oligoclase (matrix) $Ab_{84}An_{11}Or_5$
5. Chromite (inclusion in olivine)

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"...a small fish in a small pond..." The Reverend W.B. Clarke (1798-1878): 200 Years on (Part I)

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(Communicated by D.F. Branagan)

Abstract: The Reverend W.B. Clarke remains an enigma in the annals of Australian science, despite the publication of numerous books and articles on his life and times. This is due to the deficiencies of previous researchers in addressing the full gamut of the Reverend gentleman's work. Though the basic details of Clarke's life are well known, numerous significant gaps exist in the surviving archive. For example, his personal collection of rocks and fossils, along with geological maps and library, were all destroyed in the Garden Palace fire of 1882. Furthermore, the large corpus of published work which appeared in Australian newspapers between 1839-78 has only recently been identified, and his personal correspondence awaits 'translation' and publication. Until these primary sources are studied in detail, the jury must remain out as to whether W.B. Clarke deserves the title of 'Father of Australian Geology' or any similar accolade.

INTRODUCTION

1998 marks the 200th anniversary of the birth of William Branwhite Clarke in the village of East Bergholt, Suffolk, England, at 6 pm on Saturday, 2nd June 1798. It is perhaps a fitting occasion on which to look again at the man widely known as 'the Father of Australian geology', and reassess his place in the annals of Australian science. What did Clarke actually do? We know of the substantial body of work which he published between 1828-78 (Organ, 1994), however, many questions concerning his life remain unanswered, or unanswerable. What significant discoveries did Clarke make during his lifetime? What were his achievements - on a local, national and international scale? Does he deserve the title 'Father of Australian geology'? How did he go about his work, and what influenced him to take the path he did? What was the relationship between his religious duties and scientific researches?

Clarke remains something of an enigma, despite the publication of numerous books and articles on him, most notably those by Tate (1894), Warung (1895), Jervis (1944) and Grainger (1982). Unfortunately, many of these publications, whilst rich in detail, are deficient either in their analysis of Clarke's work as a scientist and cleric, or in failing to adequately address the many facets of his life. This latter task is no easy matter, for Clarke was a man of many talents: poet, journalist, reviewer, traveller, explorer, minister, museum curator, magistrate, school teacher &

Fig. 1 Reverend W.B. Clarke c. 1840 (Mitchell Library).

headmaster, meteorologist, palaeontologist, naturalist, anthropologist, geologist, artist, writer and critic. He was also a husband, father and grandfather.

A prolific letter writer - 'he wrote too much to write brilliantly" (Warung, 1895) - and stirring orator, at least from the pulpit, our surviving impression of the man is largely the result of what has come down to us from his pen, and less so due to reportage of his involvement in public affairs. These sources reveal Clarke not as a great leader or brilliant scientist, but more an indefatigable worker, playing an important role in the development of organizations such as the Australian Museum, the Free Public Library of Sydney, and the Royal Society of NewSouth Wales; all the while carrying out a large body of original research - collecting, listing, describing, corresponding, reading, and preparing material for publication.

Self-opinionated and self-centred, upon his arrival in Sydney in 1839 Clarke focused his energies on matters geological. Any research in the Colony would, of course, have to fit in with his duties as a breadwinner and cleric. These latter two areas proved a constant distraction from scientific pursuits, causing him in 1842 to bemoan to his old friend, the Reverend Prof. Adam Sedgwick, that: 'all I want is time and means and I would then do for Australia what you and Murchison have been doing for England' (Clarke, 1842).

Somewhat frail of health - rheumatic fever was one of the reasons for his travelling to Australia - Clarke suffered a mild stroke in 1856, and again in 1878, just two months prior to his death. Parishioners loved him (Walker, 1996), yet many in Sydney society loathed him for his outspoken self-righteousness. Despite being a minister of the Church and strong advocate for universal education - pronouncing shortly after his arrival in Australia that 'to deprive instruction ... is to neglect the commands of God' (Clarke, 1840) - in 1865 Clarke was nevertheless willing to throw the young school teacher Eliza Davis out in the cold when she dared set up a non-denominational school within the boundaries of his North Shore parish (Ward, 1994).

Devoted to pursing and promoting the earth sciences in Australia at every opportunity, Clarke at times saw fit to hinder the efforts of fellow workers in the field, most notably Samuel Stutchbury (Branagan 1978 & 1992) and Robert Brough Smyth (Darragh, 1977). Acutely aware of his professional isolation in Australia - a land he referred to in 1840 as 'this wide and dreadful wilderness of sin' (Clarke, 1840) - Clarke sought out the visiting American geologist James Dwight Dana in 1839-40, yet was standoffish to the Polish scientist and explorer P.E. Strzelecki during the same period. In Clarke we therefore have a puzzling figure - a man at once endearing and inspiring, yet also petty, small-minded, prickly, jealous of competition, and prone to faults of temper and discretion. All in all, a most interesting character.

LIFE AND TIMES

The basic details of Clark's life are known from the work of previous biographers, yet many aspects remain shrouded in mystery. For example: What precisely did his geological fieldwork entail? How did he maintain both parish responsibilities and scientific work? Who were his collaborators, his confidants, his friends and enemies? At the end of the day, and two centuries on from his birth, no clear picture exists of Clarke's lifework and scientific legacy. Like so many scientists before and since, his discoveries were often outmoded, outdated, and forgotten within a generation. New researchers and workers in the field such as Richard Daintree, C.S. Wilkinson and Robert Etheridge Jnr. came along and either built upon the foundations already laid, or cast them aside as irrelevant or erroneous. For example, whilst he was able to prove the existence of Silurian formations in Australia during the 1840s, almost immediately there was the need to further subdivide that geological period. As a result, much of what Clarke revealed of a scientific nature during his lifetime has been subsumed within the general body of knowledge on the geology of eastern Australia, making the task of identifying exactly what he did all the more difficult. Clarke's many literary works - which mostly date from the 1820s and 1830s - are likewise little known.

What, then, is Clarke best remembered for? In Europe he maintains some claim to fame as inventor of the modern geological hammer, based on an article he wrote in 1828 describing and figuring such an instrument (Clarke, 1828). By 1861 English geologist Sir Roderick Impey Murchison was citing Clarke as 'the experienced geologist of New South Wales' (Murchison,1862). Upon his death in 1878, Victorian scientist Ferdinand von Mueller labelled our subject 'the nestor of Australian philosophers' (Warung, 1895), while Robert Etheridge Jnr. had no qualms in promoting him as the 'Father of Australian Geology' (Etheridge Jnr., 1878). This latter title has stuck, featuring in the two substantial biographies by Jervis and Grainger. However, geologists in States other than New South Wales now question the relevance of this accolade, especially as the widespread network of geological workers in Australia during the nineteenth century is revealed.

Clarke is frequently mentioned in works which discuss the discovery of gold in Australia, though Edmund Hammond Hargraves remains holder of that title in the mind of the general public, and in the history books (Silver, 1986). Clarke is also remembered by the Anglican Church of New South Wales as one of its pioneer clergy. Beyond this, his star has waned in recent years. Even New South Welshmen such as the late T.G. Vallance have been critical of his scientific reputation (Vallance, 1981). As a result, Clarke is now regarded by many as a second level geologist - competent and skilful, though intellectually limited. The claim that, if he had of stayed in England, Clarke would have gone on to stand beside Sir Roderick Murchison, Adam Sedgwick and Joseph Beete Jukes as a first rate geologist (Warung, 1895), is now treated with some skepticism.

The passage of time can tarnish the reputation of any public figure, and Clarke is no exception. For example, his promotion during the 1850s of the theory that gold was to be found on the edges of north-south trending mountain ranges is shown as an example of his intellectual limitations, though his statements regarding the effects of forest vegetation upon climate - dating from the 1830s and reiterated during the 1870s (Clarke, 1877) - preempt the Greenhouse debate and ring true to this day. As a geologist, Clarke had real difficulties in sorting out the true age of the New South Wales coal measures, though with persistence and the help of local and overseas colleagues such as James Dwight Dana, William Sharp Macleay, Richard Daintree, Frederick McCoy, Laurent Guillame de Koninck and Ottokar Feistmantel, he was able to get it right in the end (Vallance, 1981). Whilst this may be seen as a failing on his part, others could suggest that it reveals his willingness to work collaboratively and to accept rational argument, even if it should prove him wrong along the way.

In reassessing Clarke's life and work we need to go back to the primary sources: the manuscript diaries and letters, maps and plans, drawings, collections of rocks and fossils, published works such as books, pamphlets and articles in scientific journals and newspapers of the day. Consider also the opinions of peers, fellow workers in the field, and contemporaries. Take on board assessments made since his death by biographers and commentators. It could be argued that all of this has been done, and that the judgments have been made, based on the wealth of material available on Clarke since the time of his death in 1878; that his life is an open book, with little of interest left unrevealed. Yet, just as the Charles Darwin industry continues to rewrite the biography of that famous scientist on what seems like a yearly basis, so too it could be said that the full story of the life and times of the Reverend W.B. Clarke is yet to be told. Known or unknown to previous biographers and discussants, there are many pieces missing from the puzzle which is the life of the Reverend W.B. Clarke.

MISSING LINKS - LETTERS, MAPS & NEWSPAPERS

In studying the work of any scientist, we look to the details of their everyday existence - we seek out biographical information, attempt to understand the day-to-day methods of their profession, the environment in which they worked; assess individual knowledge base and technique, review the results of individual and collaborative endeavour. Fortunately, in the case of Clarke, much of this detail may be gleaned from his extant correspondence, a large collection of which is located in the Mitchell Library, Sydney (Moyal, 1994). His many publications are also strongly biographical, providing precise details on the development of his science. The correspondence collection is perhaps the richest source of information on Clarke and his colleagues, however it has its limitations. The Mitchell Library material has only been consolidated and available to researchers since the 1960s, whilst a concise listing did not appear until the 1980s. The correspondence therein is mostly inwards, with those important letters Clarke wrote to colleagues such as Roderick Murchison and Adam Sedgwick remaining largely unknown and inaccessible in overseas collections until recent years. Furthermore, we still await 'translation' (Clarke's handwriting is very difficult to read) and publication of the more significant items from this important archive. His few books, most notably *Researches in the Southern Goldfields* (1860) and *Remarks on the Sedimentary Formations of New South Wales* (1878), are scarce and barely reveal the true extent of his writing, though all are significant in recording the Reverend gentleman's exploits and presenting his findings. The large corpus of Clarke-related material located in Australian newspapers such as the *Sydney Morning Herald* and the *Australian* has also been neglected in the past (Organ, 1992). Lord Macaulay's famous observation that 'the only true history of a country is to be found in its newspapers', can perhaps here be applied to the life of Clarke, at least in part.

An event of some significance in our study is the Garden Palace fire of 22 September 1882. This catastrophe caused the destruction of a significant archive, including Clarke's personal collection of rocks, fossils, minerals, geological maps and library, all of which had been purchased by the New South Wales government in 1879 for £7000. The loss of this material undoubtedly affects our current view of Clarke, making it all the more difficult to appreciate the many accolades he received during his lifetime and upon his death. The true scale of this loss is revealed if we look, for example, at Clarke's collection of geological maps, and to other evidence of his work in this area, such as field notes and stratigraphic columns.

Detailed mapping and the compilation of accompanying notes are vital processes in any geologist's efforts to develop a stratigraphic profile of an area under investigation. Yet, it has been noted that there are no significant geological maps in Clarke's Mitchell Library collection, or anywhere else for that matter (Darragh, 1977; see also Branagan, 1984). How can we reconcile this with the fact that, during his lifetime, Clarke was labelled the 'William Smith of Australian Geology', in reference to that great British field geologist and pioneer of biostratigraphy and the stratigraphic column? We know Clarke placed due importance on the acquisition of field data, and proudly boasted of his many years working alone in the field, compiling such information. He was also openly critical of 'closet geologists' such as Frederick McCoy who, in his opinion, relied too heavily on palaeontological findings when making age determinations, often disregarding relevant stratigraphic information (Clarke, 1878). It therefore seems logical that Clarke would have built up a substantial collection of geological maps and stratigraphic columns during his more than six decades as a practising geologist. Yet such a collection does not appear to exist, with Darragh suggesting it may never have existed in any substantial form, 'in part owing to the reconnaissance nature of much of [Clarke's] work' (Darragh, 1977). Such an assessment does not sit easy with what we know of the way in which Clarke worked.

Part of the answer to this mystery lies with the Garden Palace fire of 1882. The geological maps destroyed in that inferno, and of which no detailed listing is known, most likely formed the bunk of Clarke's collection. As a result, we are only able to assess his work in this area from the few maps published during his lifetime, and the geological map of New South Wales issued in 1880, two years after his death (Clarke & Wilkinson, 1880). Unfortunately, this latter significant work gives a distorted view, for it was seen through the press by C.S. Wilkinson,New South Wales Geological Surveyor, and incorporated the work of other geologists associated with the Survey. Apart from this item - which represented to Clarke the culmination of almost 40 years mapping the geology of New South Wales - the extant manuscript and published material does not provide much of a picture of Clarke's skills in mapping, or enthusiasm for the task. Without a substantial map collection to work on, we are left with precious little evidence to support Clarke's claim to having geologically investigated more than 100,000 square miles of eastern Australia between 1839-78. The loss makes it difficult to trace with any precision the actual extent of his fieldwork, to locate specific fossil localities, and to analyse the ongoing development of his delineation of the sedimentary formations of New South Wales.

WHAT DID CLARKE ACTUALLY DO?

Though there are significant gaps in the Clarke archive, a great deal nevertheless survives, and, as a result of research to date, we can roughly divide his life into two phases: England and Europe 1798-1839; and New South Wales 1839-78. During the first period Clarke was raised and educated, growing up in the village of East Bergholt, Suffolk, the son of the local schoolmaster. The Clarke family lived just around the corner from the ancestral house of the great British landscape artist John Constable (1776-1837), with the Constables in later life remembering our subject as the 'young Billy Clarke' (Beckett, 1962).

After leaving school, William worked as a teacher and schoolmaster, before accepting a ministry in the Church of England. He simultaneously pursued an interest in the arts and literature, publishing a number of collections of poetry during the 1820s. Whilst at Cambridge University between 1817-21 he studied under Dr. E.D. Clarke and attended the lectures of Professor Sedgwick, therein developing a passion for natural history and the new science of geology. His initial focus on meteorology and zoology was replaced by geology and palaeontology during the 1830s. From the early 1820s Clarke had carried out fieldwork in England and on the Continent, slowly developing his skills in this area. During that decade he visited the coalfields of Staffordshire and Derbyshire (1821); the Chalk, Oolitic and Tertiary districts of Yorkshire and Lincolnshire (1823); the Chalk districts of Sussex and Normandy (1824); southern France, the Alps and northern Italy (1825); the Netherlands (1826-7); Prussia and Holland (1827); Belgium, the Ardennes and the Tertiary districts of Nassau (1828); the volcanic districts of the Rhine and Moselle (1829); and the Chalk and older formations of the frontiers of France and Belgium (1830). With the coming of the new decade he fell in love, was scorned, and later married another. He began to raise a family, and after 1833 developed his parish of St. Mary Longfleet, Poole, Dorsetshire.

From 1828 through to 1839 Clarke was a prolific contributor to journals such as the *Magazine of Natural History*, and began submitting pieces to the Geological Society of London in 1837. Whilst continuing to visit the continent during the 1830s, his geological investigations were mainly centred on England. A major study of the geology of southeastern Dorsetshire was published in the *Magazine of Natural History* at the beginning of 1839. These early geological treatises reveal Clarke as an active member of that distinctly English school of historical geology which, by 1830, was primarily interested in palaeontology and stratigraphy. Those other branches of the science such as mineralogy, igneous petrology and economic geology were of secondary concern only, and in some instances even considered below the dignity of real geologists and best left to local mineral surveyors (Rupke, 1983). Individuals such as William Buckland at Oxford University and Adam Sedgwick at Cambridge were at the head of this movement. Both were Church of England ministers, reflecting 'the indigenous tradition ofAnglican learning in which natural and revealed religion were intimately interwoven with the form and substance of science.' The new field of geology therefore sat easy with clerics such as Clarke, and was in many ways enthusiastically embraced by them. This is evidenced by the large network of scientifically literate parsons which sprang up throughout England during the first half of the nineteenth century.

By the end of the 1830s the die had been cast - Clarke's life had settled into a pattern of carrying out scientific researches, whilst fulfilling his duties as husband, father and cleric. Towards the end of the decade he became restless and, looking for a healthier climate and improved prospects for himself and his family, decided to emigrate to Australia. Upon arrival in New South Wales on 27 May 1839 he was no longer a young man. Now entering his forties, and with young children to support, he had matured and attained confidence in his own abilities. With the knowledge gained from almost twenty years experience as a geologist behind him, he enthusiastically took to the task urged upon him by the Reverend Adam Sedgwick the previous year, namely, to delineate the sedimentary formations of the Colony and report back to England. Though often sidetracked over the next forty years by family and clerical duties, he saw to it that the task given was completed to the best of his abilities by the time of his death in 1878, during his eightieth year.

AUSTRALIA AND THE BUSH

Ever the man with a mission, Clarke, as soon as he was able upon arrival in the Colony, began fieldwork about Sydney. He travelled south to Illawarra in 1839-40 with American James Dwight Dana, westward over the Blue Mountains the following year, and further afield as the decade progressed. His letters to Sedgwick and Murchison from this period describe the activities of our travelling parson as he built up his knowledge of the local geology, collected numerous rocks and fossils, and consolidated his thoughts in the light of overseas developments. A list of localities associated with the 2673 rocks, fossils and minerals Clarke sent to Sdgewick in November 1844 (Table 1) points to the extent of these initial excursions.

It is unclear whether Clarke personally collected all this material, or acquired some of it from fellow collectors and institutions such as the Australian Museum. Whatever the truth, this somewhat frantic pace of collecting was perhaps motivated by the thought that he would return to England in the short term. Of course, this was not to be the case, and he remained in the Colony until his death in 1878. The first few years in New South Wales also proved somewhat turbulent for Clarke - the effects of economic depression were widespread, he worked briefly as headmaster of the King's School, Parramatta, and his family sailed for England at the beginning of 1842, not to return until 1856. By 1843 his life had settled into a pattern of exchanging parishes to facilitate fieldwork, collecting specimens for dispatch to England, and publishing his findings in local newspapers such as the *Sydney Morning Herald*. Articles also appeared in overseas journals during this period, however they were often edited down, omitting illustrations such as maps and drawings, or substantial sections including listings of individual fossils. Articles could take months, or even years, to get to press, relying as they did on the goodwill of Clarke's correspondents in presenting them to bodies such as the Geological Society of London and the Geographical Society.

It was between the years 1840-56 that Clarke was most active in the field. Not only did he walk over and travel through a large part of eastern New South Wales, but he was alsoinvolved in official government surveys of the goldfields to the north and south of Sydney between 1851-6, and visited Tasmania, Victoria and southern Queensland on a number of occasions. All of this work added to his store of local knowledge, and though precise ages for individual formations would as ever prove elusive and cause him to rely upon the opinions of overseas experts, he nevertheless quickly developed an understanding of the basic geological structure of the settled portions of the Colony. This was achieved through collecting rocks and fossils and studying the publications of previous workers in the field, finding much of relevance in the journals of explorers such as Thomas Livingstone Mitchell and Ludwig Leichhardt (Webster, 1980). Clarke also built up a network of associates - mostly interested amateurs - who would provide him with specimens and information. In some instances he employed them to search for fossils in inaccessible areas such as southern and central Queensland (Clarke, 1861).

By the end of 1854 Clarke was able to mount an exhibition of New South Wales rocks and fossils in the newly opened Australian Museum building. For the first time, a detailed stratigraphic column revealing the geological history of the Colony was laid out for all and sundry to view, by way of 435 individual rock, fossil and mineralogical specimens. A brief catalogue of the material contained therein was also published (Clarke, 1854). Unfortunately the collection and its

Table 1: List of Rocks, Fossils, and Minerals, sent to Professor Sedgwick and deposited in the Woodwardian Museum, Cambridge. Forwarded November, 1844. {a: auriferous; c: carboniferous; t: tertiary; v: volcanic} (Clarke, 1878, Appendix lll)

Locality	No.	Type	Locality	No.	Type
Hawkesbury District	115	c	Gill's Cliff	18	c
Wianamatta District	271	c	Bathurst section	79	
Prospect	22	c	Sutton Forest and Mittagong	24	c & t
Matavai	5	c	Mount York	2	c
Piakibaba	33	c	Upper Hunter	19	c
Maroota	16	c	Twofold Bay and Maneroo	16	a
Illawarra	588	c	Page	24	c
Stonequarry	6	c	Wollombi G. Plains, &c.	10	c
Awaaba	31	c	Mudgee, &c.	47	a
Hartley, Cox's River, &c.	34	a	Newcastle and up to Loder's Creek	111	c
Arriwa and Irrawang	38	c	Paterson District and Stroud	12	c
Harpur's Hill	5	c	Lewin's Brook	18	c
Mudgee	33	c	Williams River	65	c
North of Liverpool Range to Peel	54	a	Hunter River	34	c
Clarence River, and north of	18	c & a	Binjaberri	44	c
Argyle	145	a	New England	33	a
Murrumbidgee	71	a	Harpur's Hill	20	c
Murray	119	a & t	Darlington	16	c
Port Stephens	55	c	Mitchell's River, Glendon, &c.	75	c
Norfolk I.	6	v	Korinda	38	c
Windsor	1	c	Segenhoe	33	c
Muswellbrook	47	c	Richmond and Moreton Bay	51	c
Cedar Brush	23	c			
Mt. Wingan	34	c	**Total**	2,673	

accompanying catalogue largely went unnoticed, despite travelling to the Paris International Exhibition the following year.

Throughout his time as a resident of New South Wales, Clarke played an important role as a focus for all matters geological, acting as a publicly accessible storehouse for information and collections. Rocks and fossils would be sent to him from all parts of the Colony for identification, or to be dispatched to Europe for further study, while the local press was utilised to report new discoveries. We can garner an idea of the way Clarke worked by looking at his treatment of fossil trilobites.

THE TROUBLE WITH TRILOBITES

Trilobites are well known Palaeozoic marine arthropods, with distinct 3-part outer shell (carapace) composed of the head (cephalon), body (thorax) and tail (pygidium). They are common in the Silurian. When Clarke arrived in New South Wales in 1839 local specimens were unknown. Therefore, spurred on by the publication that year of the first edition of *The Silurian System* (Murchison 1839), he set about the task of identifying these important fossils locally. Such a discovery would not only assist Murchison in proving the global extent of the Silurian, but also substantiate the existence of Palaeozoic formations in Australia.

On 2 December 1842 Clarke identified numerous moulds of trilobites (genus *Trinucleus*) at two localities in the upper Hunter region - within a sandy micaceous mudstone at Burragood (Dunvegan) on the Paterson River, and in a limestone on the left bank of nearby Binjaberri Creek, a tributary of the Allyn River. Reference to these discoveries was made in a note published in the *Sydney Morning Herald* on 6 April 1843:

> "We are also informed that Trilobites ... have since been discovered in this colony by the Rev. W.B. Clarke, and that two or three species associated with other undoubted Silurian fossils have been made out by him. That gentleman has, therefore, the good fortune of having detected the first actual proof of the relative age of the Australian series of rocks, and of satisfactorily determining that they are of the palaeozoic era... (Clarke, 1843)"

In November 1844 Clarke despatched to Sedgwick his consignment of some 2673 rocks, fossils, and minerals for identification and deposition in the Woodwardian Museum, Cambridge. Included amongst the collection were trilobite specimens from Burragood and Binjaberri Creek. Clarke returned to the upper Hunter region in January 1845 and located further *Trinucleus*, along with species of *Asaphus* at Trevallyn on the Paterson River and at Colo Colo on the Allyn. William Sharp Macleay subsequently named one of these species *Trinucleus clarki* after its discoverer (Clarke, 1848).

Meanwhile, during January-February 1840 the visiting Polish scientist and explorer Count P.E. Strzelecki had found 'small oblong impressions resembling Trilobites' in the Yass Plains area, whilst travelling overland from Sydney to Port Phillip (Strzelecki, 1845). Following the Count's return to England in 1843, fossils associated with these trilobite casts were viewed by Murchison and studied in more detail by English palaeontologists John Morris and William Lonsdale. They were allocated a Devonian age, though the individual trilobite species were not identified. This information was published in Strzelecki's *Physical Description of New South Wales and Van Dieman's Land*, which appeared in London during the middle of 1845. The author sent a copy to Clarke, and he reviewed it warmly within the *Sydney Morning Herald* during March 1846. Two months later (May 1846), Strzelecki's friend Philip Parker King showed Clarke a rock containing trilobites (*Trinuclei* and *Asaphus*). It had been collected by T.A. Murray at Yarralumla near Canberra, on the northern bank of the Murrumbidgee River. Strzelecki's Yass Plains were located just 32 miles to the north-west, and most likely associated with the same formation.

These trilobite discoveries from the southern districts of New South Wales stirred Clarke into action. He immediately set about consolidating the information then available, and on 26 May 1846 completed an article 'On the Occurrence of Trilobites in the Protozoic Rocks of New South Wales' for submission to the *Tasmanian Journal of Natural Science* (Clarke, 1849). This was subsequently rewritten early in 1847 and sent off to the Geological Society of London. It was presented to that learned body on 16 June 1847 and published in its *Quarterly Journal* the following year (Clarke, 1848). Therein Clarke went beyond merely announcing the discovery of Australian trilobites. He suggested that 'the beds furnishing the Trilobites of the Paterson and Murrumbidgee are related more nearly to the Silurian than to the Devonian rocks of Europe.' This argument was in opposition to the age given in Strzelecki's book (Devonian) for the Yass Plains materiaL Clarke also mentioned Ludwig Leichhardt's discoveries of Silurian fossils in the Burdekin

River area of Queensland during 1842-3, thereby suggesting the presence of the formation along the entire length of the Australian cordillera, or Great Dividing Range. Such information was gratefully received by Murchison, who incorporated it within the later editions of his book on the Silurian.

Clarke's concise 1847 article on Australian trilobites was typical of the way in which he wrote - it was introduced by an historic summary of what had been published to date on the topic, followed by the presentation of precise information on his own discoveries and a discussion of the significance of the find in regards to the ongoing researches into the age of the local strata. Both lithological and stratigraphic information was also supplied. A list of some 240 fossil species associated with the Burragood trilobites and included with the original 1847 manuscript did not appear in the final Geological Society article. Also lacking were precise palaeontological

Table 2: Australian Trilobite Species Collected by the Rev. W.B. Clarke 1842-78

Name	Location	Reference
Asaphus	Burragood, Paterson River	Clarke 1847, 64
Brachymetopus strzelecki	Burragood, Paterson River	McCoy 1847, 229-31
	Glen Williams	De Koninck 1898, 280-1
Bronteus goniopeltis	Rock Flat Creek	De Koninck 1898, 46-7
Bronteus partschii	Boree Cavern, Wellington	De Koninck 1898, 45-6
Calymene blumenbachii	Bowning, Yass	De Koninck 1898,44
	Yarralumla	Salter 1856
	Yarralumla	De Koninck 1898,44
Calymene macleayi	Yarralumla	Salter 1856
Cheirurus insignis	Yarralumla	De Koninck 1898, 38
Cromus bohemicus	Yarralumla	De Koninck 1898, 42-3
Cromus murchisoni	Quedong	De Koninck 1898, 43
	Yarralumla	De Koninck 1898, 43
Encrinurus barrandei	Yarralumla	De Koninck 1898, 40-2
Encrinurus punctuas	Duntroon	De Koninck 1898, 39-40
	Yass	De Koninck 1898, 39-40
Griffithides eichwaldi	Upper Williams River	De Koninck 1898, 278-80
Harpes ungula	Rock Flat Creek	De Koninck 1898, 47
Illaenus wahlenbergi	Borre Cavern, Wellington	De Koninck 1898, 36
Lichas palmata	Rock Flat Creek	De Koninck 1898, 45
Phillipsia ?gemmulifera	Burragood, Paterson River	McCoy 1847, 221
Phillipsia seminifera	Dunvegan	De Koninck 1898, 276-8
	Burragood, Paterson River	De Koninck 1898, 276-8
	Colo Colo,Allyn River	De Koninck 1898, 276-8
Proteus stokesii	Yarralumla	De Koninck 1898, 44-5
Staurocephalus clarkei	Rock Flat Creek	De Koninck 1898, 36-38
Trinucleus	Burragood, Paterson River	Clarke 1847, 64
Trinucleus caractaci	Yarralumla	Clarke 1847, 66
Trinulleus clarkei Macleay	Burragood, Paterson River	Clarke, 1847, 64

descriptions of the various Australian trilobites. In this, Clarke was waiting upon his friend Sedgwick.

Whilst Clarke was consolidating his thoughts on these local fossils and their place within the Palaeozoic formations of eastern Australia, back in England work had begun on describing some of the fossils among the material sent there in 1844. The task was allocated to Sedgwick's palaeontologist Frederick McCoy, who, during the course of his investigations,identified a new trilobite genus and species, which he named *Brachymetopus Strzelecki*, along with two species of *Phillipsia*. McCoy's findings were published in the *Magazine of Natural History* at the end of 1847 (McCoy, 1847). They reached Australia by the middle part of the following year, and Clarke saw to it that this material was then made known locally, via the columns of the *Sydney Morning Herald* (21 December 1848 - 16 March 1849), the *Tasmanian Journal of Natural Science* (1849) and the *Proceedings of the Royal Society of Van Dieman's Land* (1851). Though McCoy's descriptions were detailed and revealed his skills as a palaeontologist, Clarke was somewhat miffed at the ascription of a Carboniferous (oolitic) age to the coal flora and associated fauna, in opposition to stratigraphic and field evidence which was suggestive of a much older time period.

Having brought Australian trilobites to the notice of European geologists during 1847-8, in 1849 Clarke sent a small box of specimens from Yarralumla, Colo Colo and the Paterson River to Sedgwick for identification (Wright, 1994). Apparently they were set aside upon receipt. In 1853 Murchison asked Clarke to send some Australian Silurian fossils to England, and as a result a further collection arrived there in 1855. They were subsequently studied by J.W. Salter during 1856-8, and though the results were never published, Clarke obtained a copy of his preliminary assessment (Clarke, 1878). On other fronts, Upper Silurian trilobites were located in Tasmania during 1860 by Charles Gould and described the following year, whilst Prof. McCoy also identified various Victorian species (Clarke, 1878).

By the end of the 1850s Clarke was rightly frustrated at the lack of detailed palaeontological study of the fossils he had sent to Sedgwick and Murchison between 1844-55, whilst his cool relationship with McCoy, now resident in Melbourne, meant that he could not rely on him to any degree for palaeontological assistance. Their relationship was largely one of conflict rather than collaboration, primarily centred on a disagreement on the relative ages of the Australian coalfields. The frustrations over the palaeonotological study of Australian fossils were not all one-sided. Clarke's frequent requests for results caused Englishman J.W. Salter to note in a letter to Sedgwick on 25 May 1856, that Clarke was 'a troublesome correspondent' and 'Murchison is heartedly sick of it.' Furthermore, he, Salter, 'did not mean to be bullied by any Australian into doing more until I have Wales out of hand' (Wright, 1994).

As a result of the delays and lack of cooperation by his English associates, Clarke turned to Laurant Guillame de Koninck at the University of Liège. Between 1864-76 he forwarded to him a collection of some 1000 Palaeozoic fossils from New South Wales, including various trilobite specimens. De Koninck's palaeontological descriptions were eventually published in Brussels during 1876-7, with financial support from Clarke (de Koninck, 1876-7). The resultant text was accompanied by finely detailed lithographic plates and proved a landmark in the history of Australian palaeontology, standing alongside Ottokar Feistmantel's work on the coal and plant-bearing beds of eastern Australia (Feistmantel, 1878-9) as testament to Clarke's perseverance and skills in this field. Both works were subsequently published by the Geological Survey of New South Wales (Feistmantel, 1890; de Koninck, 1898).

Clarke was never one to rest on his laurels. During 1876 he once again visited the Yass Plains area and located further trilobite specimen, working upon them right up to the time of his death. His catalogue of involvement in the discovery of various Australian trilobites is therefore substantial (Table 2). The 4th edition of his *Sedimentary Formations of New South Wales*, completed on 2 June 1878, contains an impressive set of appendices which bring together the major palaeontological discoveries of his time relating to eastern Australia.

Clarke's work with trilobites extended throughout the length of his residence in the Colony. From this brief study we see that by the 1840s he had developed the skills to locate and identify trilobite species, make appropriate lithological and stratigraphic records to assist in the dating process, and consult the literature to ensure priority of discovery. He was also adept in writing up his findings in a precise scientific manner, and presenting them for publication. Manuscript sketchbooks in the Mitchell Library also suggest he was a competent hand hand at scientific illustration (Clarke, 1843-77). As such, Clarke was an important asset to the Colony of New South Wales and the ongoing process of scientific discovery He was not alone in this task of collecting and expanding the geological frontiers, but was ably assisted by local colleagues such as William Sharp Macleay. However he did bring a decided professional edge to the task, coming from an environment in England where geological discoveries were commonplace, the geological timetable was still evolving, and there was much spirited debate in the area. The controversy over the Devonian, and the eventual rift between Murchison and Sedgwick, is clear evidence of this (Rudwick, 1985).

Clarke learnt his geology in the shadow, if not the actual company of those two great scientists, and perhaps tried to bring to the Colony some of the excitement then surrounding this rapidly advancing branch of science. The solid grounding in geology, which he had attained prior to coming to Australia, held him in good stead for the task ahead. It was noted by Prof. Smith in 1879 that Clarke's 'faculties remained unclouded to the end' (Smith, 1879). During his last few weeks, and despite suffering the effects of a stroke on 6 March 1878, Clarke was able to complete the 4th edition of his *Sedimentary Formations*, put the finishing touches to his geological map of New South Wales, arrange his fossil collection, and write a letter to de Koninck on 15 June. The evening of the following day he passed away.

(to be continued)

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Thesis Abstract: Survival Analysis Diagnostics

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Abstract of a Thesis Submitted for the Degree of Doctor of Philosophy
at Queensland University of Technology

The Cox proportional hazards model for assessing survival data continues to grow in popularity, especially in the medical context. This Thesis provides diagnostics to determine if observations are influential for the parameter estimates in the Cox proportional hazards model.

Diagnostics such as Cook's distance have been available for the ordinary least squares model for many years. In order to extend them so they can be used for the proportional hazards model it is necessary to first extend them to the generalised least squares model. For models with normal errors with known variance matrix, the change in parameter estimates that occurs when cases are removed from the dataset can be calculated exactly. For generalised least squares the change is exact if it can be assumed that the estimates of the parameters in the variance matrix do not change when cases are removed.

The Newton-Raphson fitting procedure for the proportional hazards model is an iterative procedure. If we find fully iterated estimates of regression parameters then we can take one-step of a new iterative procedure toward parameter estimates for a reduced dataset. For the proportional hazards model with the usual loglinear relative risk function, the formula used for the Newton-Raphson iterative procedure looks like the formula for calculating the exact change in the generalised least squares model.

The one-step estimates of the changes in parameter estimates for the proportional hazards model can then be used to construct quantities like Cook's distance.

This thesis shows that the data augmentation method commonly used for proportional hazards is a type of case deletion method. A new case deletion method is examined.

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Thesis Abstract: Some Cardiovascular Morphological Specialisations and Aspects of Cardiovascular Control in the Lower Vertebrates, *Carcharhinus melanopterus*, *Rhinobatos typus*, *Neoceratodus forsteri* and *Arius graeffei*[*]

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Abstract of a Thesis for the Degree of Doctor of Philosophy at the University of Queensland

Catecholamines released from chromaffin cells appear to play an integral role in the regulation of the cardiovascular system of lower vertebrates. Chromaffin cells are present in the axillary and suprarenal bodies of *R. typus* and *C. melanopterus*; in the atrium, intercostal arteries and the posterior cardinal vein of *N. forsteri*; and in the posterior cardinal vein in the head kidney of *A. graeffei*. Although chromaffin cells have been described in the sinus venosus of other elasmobranchs, there are no chromaffin cells here in *R. typus* and *C. melanopterus*. Chromaffin tissues in *N. forsteri* and *A. graeffei* exhibit tyrosine-hydroxylase-immunoreactivity. Ultrastructural studies show that chromaffin cells contain large numbers of chromaffin-positive, electron-dense, membrane-bound granular vesicles. Two cell types (presumably adrenaline- and noradrenaline-storing cells) can be distinguished on the basis of granule electron-density in *R. typus*, *C. melanopterus* and in *A. graeffei* but only one cell type can be distinguished in *N. forsteri*. Chromaffin cells receive an innervation in these lower vertebrates, and synaptic specialisations have been observed in close association with chromaffin cells.

The role of the autonomic nervous system in the regulation of the cardiovascular system is investigated. Physiological and anatomical studies failed to reveal evidence for an autonomic innervation of the branchial vasculature of *C. melanopterus*. Perfused gill preparations are responsive to noradrenaline with vasoconstriction at high concentrations and vasodilatation at low concentrations. The branchial vasculature constricts via muscarinic receptors in response to acetylcholine. The distribution of the caudal autonomic nervous system of *C. melanopterus* and *R. typus* is similar to that of other elasmobranchs.

Adrenergic nerve fibres were demonstrated histochemically. Isolated tail preparations in *R. typus* and *C. melanopterus* are responsive to perfused catecholamines and

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[*] Corrected reprint of article initially published in Vol. 131, Parts 1/2, 37-39

acetylcholine which both vasoconstrict the tail vasculature. Nerve stimulation experiments gave inconclusive results in these preparations. The functional role of the autonomic nervous system in regulating the tail vasculature of elasmobranchs remains controversial. This is the first study to demonstrate catecholaminergic nerves in the dipnoans. The pulmonary artery and branchial vasculature contain catecholamine fluorescent nerves which have the ultrastructural features of catecholaminergic nerves.

Adrenergic nerves, revealed immunohistochemically, are associated with the systemic secondary vessel system of the teleost, *A. graeffei*. Vascular casts are used to describe the systemic secondary vessel system in *A graeffei,* and some fine structural features of this system are described for the first time in this study. No morphological features of such a system are present in *R. typus*, *C. melanopterus* or *N. forsteri*. The measurement of a low erythrocyte content in the cutaneous veins of *R. typus* suggests that a functional shunting of erythrocytes could be occurring.

The four species studied share many cardiac ultrastructural features. Exposure of *R. typus* to a low salinity environment for three days resulted in some morphological and morphometric changes in myoendocrine cell ultrastructure presumably due to an increase in atrial natriuretic or related peptide production.

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Thesis Abstract: Neuroendocrine Studies on the Function of the Normal and Abnormal Human Hypothalamic-Pituitary-Adrenal Axis

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Abstract of a Thesis Submitted for the Degree of Doctor of Medicine
at The University of Queensland

This thesis reports several studies which assessed the function of the hypothalamic-pituitary-adrenal axis (HPAA) in healthy human subjects and in patients with (1) myotonic dystrophy (DM), an autosomal dominantly transmitted form of muscular dystrophy which involves multiple organ systems; and (2) post-traumatic stress disorder (PTSD), a psychiatric condition which results from exposure to a very stressful, dangerous situtation. Plasma concentrations of adrenocorticotropic hormone (ACTH), cortisol, and arginine vasopressin (AVP) were measured in response to administration of the opioid antagonist naloxone, exogenous AVP and synthetic ACTH. All studies were placebo-controlled and singleblinded.

In healthy volunteers, administration of both naloxone and AVP resulted in a synergistic ACTH response compared to administration of each agent alone, similar to the synergism previously reported between corticotropin-releasing hormone (CRH) and AVP. This finding indicates that, in humans, naloxone stimulates the HPAA predominantly or exclusively via increased release of hypothalamic CRH, similar to its mechanism of action in animal studies.

In DM patients, the ACTH response to naloxone was markedly increased compared to control subjects. Pre-treatment with nifedipine (which blocks dihydropyridine (DHP)-sensitive Ca^{2+} transport via L-type voltage-dependent Ca^{2+} channels) delayed the ACTH and cortisol responses to naloxone in the DM group without altering the magnitude of these responses. In contrast, nifedipine reduced but did not delay the ACTH and cortisol responses to naloxone in the control group. These findings suggest the presence of an abnormality of DHP-insensitive Ca^{2+} transport in the corticotrophs of DM patients. Pre-treatment with aspirin (which inhibits the cyclo-oxygenase pathway of arachidonic acid metabolism) resulted in an increased ACTH response to naloxone in the control group, but a paradoxical decrease in the ACTH response of the DM patients. This finding implies that the interaction between arachidonic acid metabolites and ACTH secretion is abnormal in DM patients. The effects of nifedipine and aspirin on the

HPAA are probably occurring at the pituitary level of the axis. The abnormal findings in the DM patients are likely to be due to altered cAMP-dependent protein kinase function in this condition.

The PTSD patients were studied by sequential injections of naloxone and AVP in separate dose-response protocols. Half of the PTSD patients had greater ACTH responses to the lowest dose of naloxone than did any of the control subjects. Detailed statistical analysis confirmed that these PTSD patients constituted a distinct subgroup, with greater ACTH and cortisol responses to naloxone than the other PTSD patients or the control subjects. However, there were no differences in the responses to AVP between the PTSD patients and the control subjects. These findings suggest that there is an abnormality in PTSD which may cause hypersensitivity to naloxone-stimulated CRH secretion, and that it is probably located at a supra-pituitary, rather than pituitary, level of the HPAA.

In conclusion, this thesis reports several findings on HPAA function in healthy control subjects, including the effects of nifedipine and aspirin, dose-response data for naloxone and AVP, and synergism (with regard to ACTH release) between naloxone and AVP. It also reports new abnormalities of HPA axis function in DM and PTSD which are probably related to the underlying pathophysiology of these conditions.

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Thesis Abstract: Establishing Very Low Speed, Disturbance-free Flow for Anemometry in Turbulent Boundary Layers

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Abstract of Thesis submitted for the Degree of Doctor of Philosophy,
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The thesis addresses problems encountered when establishing the very low air-flow speeds required for experimental investigations of the mechanisms of low-Reynolds-number boundary-layer turbulence. Small-scale motions in the near wall region are important features of turbulent boundary-layer dynamics, and, if these features are to be resolved by measurements in air with conventionally-sized hot-wire probes, a well-behaved canonical turbulent boundary layer must be developed at free stream flow speeds no higher than 4 m/s. However, at such low speeds, the turbulent boundary layers developed on the walls of a wind tunnel are very susceptible to perturbation by non-turbulent time-dependent flow structures which are produced in the laminar flow upstream of the test section.

Four different non-turbulent flow structures have been identified. The first is a result of quasi-two-dimensional separation of the laminar boundary-layer from the surfaces of the wind-tunnel contraction. Potential flow simulations show that susceptibility to this form of separation is reduced by increasing the degree of axisymmetry in the cross-section geometry and by decreasing the streamwise curvature of the concave surfaces. The second source of time-dependence in the laminar boundary-layer flow is an array of weak stream wise vortices produced by Görtler instability. The Görtler vortices can be removed by boundary-layer suction at the contraction exit. The third form of flow perturbation, revealed by visualisation experiments with streamers, is a weak large-scale forced-vortex swirl produced by random spatial fluctuations of temperature at the wind-tunnel inlet. This can be prevented by thorough mixing of the inlet flow; for example, a centrifugal blower installed at the inlet reduces the amplitude of temperature nonuniformity by a factor of about forty and so prevents buoyancy-driven swirl. When subjected to weak pressure gradients near the start of a wind-tunnel contraction, Görtler vortices in laminar wall layers can develop into three-dimensional separations with strong counter-rotating trailing vortices. These trailing vortices are the fourth source of unsteady flow in the test-section. They can be suppressed by a series of appropriately located screens which remove the low-speed-streak precursors of the three-dimensional separations. Elimination of the above four contaminating secondary flows permits the development of a steady uniform downstream flow and well-behaved turbulent wall layers.

Measurements of velocity in the turbulent boundary layer of the test-section have been obtained by hot-wire anemometry. When a hot-wire probe is located within the viscous sublayer, heat transfer from the hot-wire filament to the wall produces significant errors in the measurements of both the mean and the fluctuating velocity components. This error is known as wall-proximity effect and two successful methods are developed for removing it from the hot-wire signal. The first method is based on the observation that, if all experimental parameters except flow speed and distance from the wall are fixed, the velocity error may be expressed nondimensionally as a function of only one parameter, in the form $\Delta U^+ = f(y^+)$. The second method, which also accommodates the effect of changing the hot-wire overheat ratio, is based on a dimensional analyis of heat transfer to the wall.

Velocity measurements in the turbulent boundary layer at the mid-plane of a nearly square test-section duct have established that, when the boundary-layer thickness is less than one quarter of the duct height, mean-velocity characteristics are indistingishable from those of a two-dimensional flat-plate boundary layer. In thicker mid-plane boundary layers, the mean-velocity characteristics are affected by stress-induced secondary flow and by lateral constriction of the boundary-layer wake region. A significant difference between flat-plate and duct boundary layers is also observed in momentum-balance calculations. The momentum-integral equation for a duct requires definitions of momentum and displacement thickness which are different from those given for flat-plate boundary layers. Momentum-thickness growth rates predicted by the momentum-integral equation for a duct agree closely with measurements of the newly defined duct momentum thickness. Such agreement cannot be obtained in terms of standard flat-plate momentum thickness.

In duct boundary layers with Reynolds numbers (Re_θ) between 400 and 2600, similarity in the wake-region distributions of streamwise turbulence statistics has been obtained by normalising distance from the wall with the flat-plate momentum thickness, θ_2. This result indicates that, in contrast with the mean velocity characteristics, the structure of mid-plane turbulence does not depend on the proportion of duct cross-section occupied by boundary layers and is essentially the same as in a flat-plate boundary layer. For Reynolds numbers less than 400, both wall-region and wake-region similarity fail because near-wall turbulence events interact strongly with the free stream flow and because large scale turbulence motions are directly influenced by the wall. In these conditions, which exist in both duct and flat-plate turbulent boundary layers, there is no distinct near-wall or wake region, and the behaviour of turbulence throughout the boundary layer depends on both wall variables and on outer region variables simultaneously.

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Thesis Abstract: Molecular Recognition between DNA and CHIRAL Intercalative Metalloprobes

KYMBERLEY A. VICKERY

Abstract of a Thesis submitted for the Degree of Doctor of Philosophy,
Macquarie University, NSW, 1998

A series of ruthenium(II) octahedral complexes comprising the chiral N$_4$-tetradentate *N,N'*-dimethyl-*N,N'*-di(2-picolyl)-1R^*,2R^*-diaminocyclohexane (R^*R^*-*picchxnMe*$_2$) of the type Δ,Λ-*cis*-α-and Δ,Λ-*cis*-β-[Ru(R^*R^*-picchxnMe$_2$)-(bidentate)]$^{2+}$ [where bidentate = *bipy* (*2,2'-bipyridine*), *phen* (1,10-phenanthroline), *dpq* (dipyrido[3,2-*f*:2,'3h]quinoxaline), *phdi* (9,10-phenanthrenequinone diimine), *dip* (4,7-diphenyl-1,10-phenanthroline) *npdi* (1,2-diiminonaphthalene) and *dppz* (dipyrido-[3,2-a:2,'3-c]phenazine)] has been synthesised. Resolution into α and β stereoisomers and Λ and Δ configurational enantiomers has been carried out on the complexes containing the *phen, dpq* and *phdi* ligands. General structural analyses of the isomerically pure products were undertaken using ^{1}H NMR, circular dichroism and electronic absorption spectroscopic methods. The tetradentate was found to be non-stereospecific in its coordination to Ru(II), yielding both α and β conformational geometries for each of the bidentates used, with the exception of *npdi*, for which only the α isomer was obtained.

The complexes were designed to interact with DNA via a reversible intercalative mode, where the bidentate component functions as the intercalating chromophore and the tetradentate governs binding selectivities through helical groove contacts. The chiral recognition abilities of nucleic acids towards the diastereomeric and enantiomeric forms of the cations were investigated using various forms of DNA. Nucleic acid sources employed include calf thymus DNA, synthetic self-complementary oligonucleotide fragments, the homo- and co-polynucleotides poly[dA]·poly[dT] and (poly[dG·dC])$_2$, and plasmid as well as whole-cell bacterial DNA systems. Binding interactions were investigated by following the hypochromism induced in the visible absorption spectra of the complex cations upon addition of calf thymus DNA and selected polynucleotides. The complex-DNA adduct stoichiometries and equilibrium binding constants were determined and used to rank the intercalating ability of the different bidentate systems as *phdi* > *dpq* > *phen*. Bacterial mutagenesis activity assays were used to seek structure-activity relationships between the various α and β and Λ and Δ isomers in each of the bidentate systems. The results of these investigations correlate well with the ranking order ob-

tained from the binding constant data. Poly[dA]·poly[dT] and (poly[dG·dC])$_2$ polynucleotide forms and calf thymus were used to show that only minor nucleobase sequence selectivity exists between the four isomers of the [Ru(R^*R^*-picchxnMe$_2$)(dpq)]$^{2+}$ metalloprobes. Flow linear dichroism studies indicate the binding mode of action as predominantly intercalative for the *dpq* and *phdi* series metalloprobes, while the *phen* complexes were found to have an orientation indicative of groove binding to the host duplex. NMR studies of synthetic oligonucleotides interacting with various probe cations were used to show the main site of interaction on the complex, and their effects on the oligonucleotides. Metalloprobe self-association studies were carried out to demonstrate that significant p-stacking interactions occur in aqueous media for the cations based on the *dpq* and *phdi* chromophores.

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37-38	PhD Thesis - Chopin	Numerous errors in the names of organisms: corrected article presented *in toto* in Vol. 131, pp. 115-16.
CONTENTS	Clarke Medal (Botany)	Should read: Prof. C.B. Osmond.
	Archibald D. Ollé Prize	Should read: Dr Gerrit Neef.
	Edgeworth David Medal	Should read: Assoc. Prof. Albert Z.H. Zomaya

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Each manuscript will be scrutinized by the Publications Committee before being sent to an independent referee who will advise the Council of the Society on the acceptability of the paper. In the event of rejection, manuscripts may be sent to two other referees.

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Spelling follows "The Concise Oxford Dictionary". The Système International d'Unites (SI) is to be used, with the abbreviations and symbols set out in Australian Standard AS1000.

All stratigraphic names must conform with the International Stratigraphic Guide and must first be cleared with the Central Register of Australian Stratigraphic Names, Australian Geological Survey Organisation, Canberra, ACT 2601, Australia.

The **Abstract** should be brief and informative. **Tables** should be adjusted for size to fit the final publication, and should be numbered serially with Arabic numerals and must have a caption.

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The Society originated in the year 1821 as the Philosophical Society of Australasia. Its main function is the promotion of Science by: publishing results of scientific investigations in its *Journal and Proceedings;* conducting monthly meetings; organising summer schools for senior secondary school students; awarding prizes and medals; and by liaison with other scientific societies. Special meetings are held for: the Pollock Memorial Lecture in Physics and Mathematics, the Liversidge Research Lecture in Chemistry, the Clarke Memorial Lecture in Geology, Zoology, and Botany, and the Poggendorf Lecture in Agricultural Science.

Membership, as an Ordinary, Absentee or Associate Member, is open to any person whose application is acceptable to the Society. An application must be supported by two members of the Society, one of whom personally knows the applicant. Subscriptions for the Journal only are accepted. The Society welcomes, from members and non-members, manuscripts of research and review articles in all branches of science, art, literature and philosophy for publication in the *Journal and Proceedings*. Manuscripts from non-members must be communicated through a member.

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The Australian Republic And The Royal Society of New South Wales

D.J. O'Connor

1. ROYAL PATRONAGE

I know that some of you present this evening were born in the United Kingdom. I know that most of you have visited the United Kingdom, and I also know that some of you have visited Osborne House, near Cowes on the Isle of Wight.

Osborne House was the private residence of Queen Victoria and featured in the film *Mrs Brown*. It is a magnificent residence with lovely grounds and gardens and sweeping views across Cowes and to the English Channel.

Queen Victoria was crowned in 1837 and died at Osborne House in the 64th year of her reign. She has been the longest reigning English monarch. When she died, it was the end of an era. During her reign, France had known two dynasties and had become a republic. Spain had had three monarchs and Italy four.

The Royal Society of New South Wales is forever indebted to Queen Victoria. In 1866, she granted sanction to the Society's use of the title "Royal" and when advice was received from Downing Street in December 1866, the then Philosophical Society of New South Wales adjourned as the Royal Society of New South Wales. Its President was the Governor Sir John Young with the Reverend William B.Clarke as Vice President.

In his Presidential Address on 1 May 1901, one of the "founding fathers" of the Royal Society of New South Wales, Professor Liversidge, reported on what he described as a most important event(1). On 22 January 1901, the venerated sovereign, Her Most Gracious Majesty Queen Victoria died at her private residence at Osborne House on the Isle of Wight. "I ... as your representative forwarded through the kind office of His Excellency the Governor General, a telegraphic message of condolence to His Majesty the King and Royal Family; to which an appreciative reply has been received from His Majesty."

Professor Liversidge went on to say "... we wish to respectfully offer to His Majesty our loyal congratulations upon his accession to the throne and our cordial wishes that his reign ... may be characterized like that of Her Late Majesty, by marked progress in the advancement of science, literature and art, and in the amelioration of the condition of the people."

Certainly in 1901 the bonds between the Royal Society and the monarchy were quite strong. However, bonding and affiliation have decreased over the last century.

Queen Victoria was survived by six children, including four future sovereigns – Edward VII (1901-1910), George V (1910-1936), the uncrowned Edward VIII (Duke of Windsor 1936), and George VI (1936-1952). George VI was succeeded by his eldest daughter, the present Queen Elizabeth II.

Edward VII – died May 1910
In his 1911 Presidential Address, Sir Edgeworth David(2) made no reference to the death of Edward VII or to the accession of George V.

George V – died January 1936
In his 1936 Presidential Address, Dr Penfold(3), Curator of the Sydney Technological Museum, made no reference to the death of George V or to the intended accession of Edward VIII.

Edward VIII – abdicated December 1936
In his 1937 Presidential Address, Dr Booth(4), a geophysicist, made no reference to the abdication of Edward VIII or to the accession of George VI.

George VI – died February 1952
In his 1952 Presidential Address, the late Professor Bosworth(5), did refer to the "tragic news of the death of His Well-Beloved Majesty King George VI." Professor Bosworth reported that on behalf of Members and Council, he had sent a letter to Her Majesty Queen Elizabeth expressing the Society's respectful sympathy.

Queen Elizabeth II (1952 –)
There is no message of congratulation to the present Queen in the 1953 Address by President Magee (6).

Also no message of condolence was forwarded to the Palace by the Royal Society on the occasion of the tragic death of Princess Diana in 1997.

I have used this material from Presidential Addresses to show that the strength of affiliation of the Royal Society with the monarchy is not now terribly strong.

Of course, it is a source of some pride to the Royal Society that the Society has as its patrons His Excellency the Honourable Sir William Deane, Governor General, and also His Excellency the Honourable Gordon Samuels, Governor of New South Wales.

The Society really has only little contact with its two Vice Regal Patrons.

The Society's office forwards copies of our *Journal and Proceedings,* our Monthly Bulletins, our Summer School Booklets, and occasional special publications to both the Governor General and the Governor. Also we generally meet with the Governor at Kurnell on 29 April each year on the anniversary of the landing of Captain Cook.

The Society has indeed been fortunate to have the Governor General or the Governor as its guest at our Annual Dinner on infrequent occasions.

2. FEDERATION – 1 JANUARY 1901

A study of the papers and Presidential Addresses in the Society's *Journal and Proceedings* in the 2-3 years prior to and after Federation on 1 January 1901, shows that the Society was active in a wide range of scientific matters affecting the Colony and the then new State of New South Wales, but much less so in matters related to Federation and the creation of the Commonwealth of Australia.

Professor Liversidge was well ahead of his time when he proposed the formation of an Australian Academy of Science, operating under rules like those of the Royal Society of London with an elected membership. He proposed that the seat of the Academy would "… be in the Federal Capital when built where a suitable site should be reserved."

In the 1898 Presidential Address by Deane (7) and the Anniversary Address delivered by the 1899 President Mr Knibbs (8), there were no references or discussions relating to the establishment of the Commonwealth of Australia.

The 1900 Anniversary Address by the President Mr Hamlet, Government Analyst(9), was primarily directed to sanitation and public health and the collaboration of the chemist and the engineer in solving the problems of the disposal of city sewerage.

3. AUSTRALIAN REPUBLIC

In comparison with the situation existing at the time of Federation, and to have some material included in the Society's official records, it seems desirable to make some comment about the current debate in Australia as to whether Australia should become a Republic.

Webster's Dictionary defines a republic as a state or nation in which the supreme power vests in all the citizens entitled to vote and is exercised by representatives elected, directly or indirectly, by them and responsible to them.

Clause 2, Part 1 – General of Chapter 1 – The Parliament of the *Commonwealth of Australia Act 1901* states: "A Governor General appointed by the Queen shall be Her Majesty's representative in the Commonwealth and shall have and may exercise in the Commonwealth during the Queen's pleasure, but subject to this Constitution, such powers and functions of the Queen as Her Majesty may be pleased to assign to him".

The Constitutional Convention held in Canberra in February 1998 gave the Government a clear mandate to hold a Referendum on whether Australians want a Republic(10). To be successful, a Referendum must be supported by a majority of Australians in a majority of Australian States. The goal of those in favour of a Republic is to have an Australian Head of State (man or woman) by 1 January 2001 (the centenary of Federation).

The Prime Minister has committed the Government to hold such a Referendum on 6 November 1999, and if there is a successful Yes Referendum, to implement the changes on 1 January 2001.

The Constitutional Convention addressed three questions:

1. Whether Australia should become a Republic;
2. Which Republican model should be considered in the Referendum;
3. The time frame for and circumstances affecting a change.

One hundred and fiftytwo delegates participated in the Convention. These represented a wide cross section of Australians. Half of the delegates were appointed by the Federal Government and half by the Australian people.

Three models for an Australian Republic were considered by the Convention. They were:

1. Direct election of the Head of State;
2. Election by a 2/3 majority of a joint sitting of both the House of Representatives and the Senate – the Bipartisan Appointment Model;
3. Appointment by a Special Council following nomination by the Prime Minister.
4. The Convention voted in favour of the Bipartisan Appointment Model. This model is sup- ported by the Australian Republican Movement.

The Convention also considered any consequential changes to the preamble to the Constitution, the implications for the States, the procedures for nomination of the President, his/her qualifications, appointment and dismissal, powers and term of office.

The Convention also resolved a number of relevant matters. These included:

1. The Head of State should be an Australian citizen, not a member of a political party and his/her title should be President;
2. Special consideration will need to be given to transitional and consequential matters, including provision for the continued use of the term Royal, Crown or other related term, and use of royal insignia, by non-government organisations.

Mr Malcolm Turnbull, Chair of the Australian Republican Movement(11), claims that the real question for Australians in the Referendum is whether they want an Australian citizen as their Head of State. The critical issue is not how the President of an Australian Republic should be elected, but what the President's role should be.

4. IMPLICATIONS FOR THE ROYAL SOCIETY IN THE EVENT OF A 'YES' VOTE FOR THE REPUBLIC

It is desirable to consider the consequences for the Royal Society in the event of a 'Yes' vote at the forthcoming Referendum on whether Australia should become a Republic. What will be the future status of the Royal Society? What images might be conveyed to and interpreted by the general public by the continued use of the prefix Royal? Will the change to a Republic be likely to affect in any significant way the modus operandi of the Royal Society?

It is important to understand that the prefix "Royal" is granted to an organisation by the Sovereign. In our case, it was Queen Victoria. Asher Joel(12) has stated that the prefix is granted to an organisation which "has displayed a long history of undertaking important work for the benefit of the Australian community and judged by the Queen as deserving of such a prefix in recognition of that service."

Renfree(13) states that the grant of such approval "is a very high honour and a great privilege and does not terminate with the reign of the Sovereign who bestows the mark of Royal favour." Approval is not given lightly nor is it given widely.

It should be understood that the Royal Society of New South Wales incorporates the prefix Royal, but has not been incorporated by Royal Charter, as is the case for the Royal Australian Chemical Institute (Leighton(14), O'Connor(15)). The RACI, which was incorporated in 1932, was the first scientific society to become incorporated since Federation.

The RACI, founded in 1917, is currently grappling with the question via a poll of members whether it should retain its Royal Charter or surrender the Charter and move to incorporation under Australian company law(13). Difficulties have been experienced with the content of the Charter, and the time of 15 months and the high cost to change the Charter and implement new By-Laws.

McKellar(16) of the RACI claims that the advantages of maintaining the Charter appear to be based on historical perspectives. Considerable time and effort were involved in obtaining the Royal Charter, but even though "Royal" had a special meaning in the past, "perhaps today that meaning has less significance."

The New South Wales Branch President(17) of the RACI has stated "it is inevitable that Australia will become a Republic in the not too distant future and then the "Royal" tag will be anachronistic."

Some years ago, it was suggested that the Royal Society of Queensland be renamed in more recognisable accord with its charter. One proposal was the name Academy of Science. This proposal was not accepted but a possible name change is again being considered in parallel with the Republic debate. One proposal has been for the Royal Society of Queensland to be incorporated with other bodies into a Queensland Academy of Arts and Sciences, similar to the New Zealand model (18).

In this connection, it is interesting to note that the Royal Society of London has changed its name to - The Royal Society, UK Academy of Science.

To seek advice on the consequences of a 'Yes' vote at the Referendum, I have sought the opinions of senior Federal and State politicians and the Chair of the Australian Republican Movement.

The general conclusions are that in the event of a 'Yes' vote, there will be no immediate requirement for a change in name and deletion of the prefix Royal from our name, rather the Commonwealth Government and Parliament will give consideration to the transitional and consequential matters that will need to be addressed regarding continued use of the prefix Royal by non-government organisations. It is possible the situation could change depending on any change of the constitutional links of the State of New South Wales with the Crown. But that is for the future!

We should be able to draw a parallel with other societies and groups within the British Commonwealth which incorporate the term "Royal", either by grant of a Charter or by permission to use the title "Royal".

The Royal College of Physicians of Ireland is an excellent example. The College was created as the Fraternity of Physicians in 1654(19). In 1667, King Charles II granted a Charter to the College of Physicians along similar lines to those of the London College. A new Charter was granted by William III and Queen Mary in 1692. Amongst its many activities, the College was allowed to receive the bodies of six criminals executed in Dublin each year provided the remains were buried in the College.

The Royal College acquired the premises it currently occupies in Kildare Street in Dublin in 1864. Today the College is mainly concerned with postgraduate education and the setting of standards in medical care.

The history of the Royal College of Physicians of Ireland illustrates that in spite of political difficulties in England in the 17th Century, and the oppression of religious and political freedom in Ireland in the 18th and 19th Centuries, and in spite of Ireland becoming a Republic, the Royal College continues to exist and continues to elect physicians to its Fellowship.

5. REDUCTION IN STATUS AND INFLUENCE OF THE ROYAL SOCIETY

The aims of the Society are to encourage studies of Science, Art, Literature and Philosophy, to promote the development of Science and allied disciplines, to facilitate the exchange of information amongst members of the Society and others on Science and kindred topics and to disseminate knowledge.

Throughout its 178 year history, the Society has done much to fulfil its aims by activity in diverse fields of science through meetings, symposia, publications and international scientific exchanges. The main publication has been the *Journal and Proceedings*, currently published twice yearly.

In recent years, the Society has expanded its role in the promotion of science into school education through its very successful Summer Schools for Senior Secondary Science School Students.

By these means, the Society has encouraged communication across disciplines resulting in a sharing and transfer of information and ideas.

On the other hand, the Society has been much less active in the areas of scientific and social commentary and public debate on matters related to the introduction of technology, the everyday lives of people, the environment, and importantly advice to Government.

The vitality, health and status of any society are directly related to the size of its membership and the level of activity of that membership. The Society has maintained its membership at about 300 over the last century. The population of New South Wales has increased by a factor of 4 to 5 over this period. The generally poor attendance at its Monthly Meetings has paralleled the decline in activity of the membership.

Regrettably, there has been a reduction in status and influence of the Society. May I remind you that prior to World War I, the Royal Society of New South Wales was the premier society in New South Wales and together with ANZAAS perhaps even in Australia, at least in so far as the physical sciences were concerned.

There are many reasons why there has been a decline in the status of our Society over the last 50 years. I shall mention only a few:

1. Increased specialisation in science and the growth of specialised societies and scientific journals which are available worldwide by airmail and on the internet.
2. The establishment of the two Academies – the Australian Academy of Science and the Australian Academy of Technological Sciences and Engineering.
3. The establishment of bodies such as the Australian Foundation for Science, FASTS, the Clunies Ross Memorial Foundation and the Colonial Science Club.
4. The ubiquitous influence of radio and television, and their excellent science programs, with instant penetration into millions of homes worldwide.
5. The universal use of computers and more recently the development of e-mail and the Internet. Did you know that the 1990 edition of the Macquarie Dictionary did not include the entry Internet?

6. FUTURE DIRECTIONS

It seems appropriate to consider what initiatives and actions should be undertaken by Council to reverse any further decline in the status and operations of our Royal Society. Some of these have been canvassed by the so-called Reform Committee chaired by Mr Hardie.

6.1 Passive vs. Active Society

I believe that if the Royal Society is to have a viable long term future, it must change from being a passive Society which it is essentially today by virtue of its monthly technical meetings, its special lectures, awards of prizes and medals, its rarely used library in Sydney, its monthly Bulletin and the twice yearly publication of its *Journal and Proceedings*.

It must change to a Society which is more pro-active, which has a higher public profile and which is prepared to provide quality and well researched and reasoned advice to Government. This approach has been strongly promulgated by the Royal Society of Western Australia (20). It must be prepared to speak publicly not only on scientific and technological issues but also on societal and public policy issues. It should publish position papers as the occasion demands. Many of these position papers could be published in our *Journal and Proceedings*.

The Society should continually stress the importance and usefulness of scientific knowledge to the solution of social and community issues. Many of these are relevant not only to New South Wales but also have Australia wide and often international importance.

I see no reason why the Society should not make apolitical representation to Government and to the media and to discuss controversial issues. The Society members represent a wealth of scientific experience in terms of both diversity and depth, and are able to make contributions in many areas.

It is inevitable that there will be differences of opinion among individual members, but I believe the Society should be accountable to the greater community and should be pro-active in identifying issues, discussing their impact and publishing possible ramifications and related problems.

I feel that activity along these lines could also promote more high profile business, civic and political leaders to join our Society.

6.2 Journal and Proceedings

Our *Journal and Proceedings* is an ideal media for rapid publication of papers after being subject to peer review. We should aim to publish a high quality journal that contains original research material across a range of disciplines, review papers, analysis and critique of current issues and information relevant to the State of New South Wales. The Society should not avoid papers that discuss the ethical issues of topics under debate.

The quality of production of our *Journal and Proceedings* has improved considerably in the last few years, thanks largely to the efforts of the Honorary Editorial Secretary, Mrs Krysko, a former President, Dr Branagan, and our Honorary Treasurer, Dr Evans. However, I am sure that we all agree that much more can be done both on the refereeing and editorial side and from aspects of computerised compositing and printing.

I am enthusiastic about the formation of the Editorial Committee which has been established with the initiative of our new President, Professor Baker. Terms of reference for the Editorial Committee include seeking articles for the Journal, assisting the Editor in identifying suitable referees, and improving the overall quality of the Journal. I believe the Editorial Committee will contribute much strength to the Journal and Proceedings.

I see no problem for the Society arranging sponsorship for individual issues of the *Journal and Proceedings* with appropriate acknowledgment being made.

Why should we not organise a symposium related to the Olympic Games and publish these papers in the *Journal and Proceedings* and seek sponsorship from SOCOG for this particular issue?

The Editorial Committee and Council should consider increasing availability of the Journal to a wider audience via publication on the World Wide Web. In this area, we are indebted to both our Honorary Secretary, Dr Lake, and the University of Technology, Sydney for facilitating publication of details of the Society on the Web. More extensive use of the Web would help in raising the profile of the Society.

6.3 Membership

The Society has an aging membership, with some 20% of its members being retired. Many present members of Council have retired from active full-time work.

We should attempt to recruit more young members into the Society. The future health of the Society will be determined by its present young members and those young members yet to be recruited. These are the persons who will take the Society into the new Millennium.

In this matter, it is encouraging to see the initiatives introduced by the new President and adopted by Council. Council has approved the introduction of Royal Society of New South Wales Studentships. There are prizes to be awarded to outstanding PhD candidates at New South Wales universities and who have completed at least two years of their candidature. It is hoped that sponsors can be found for the studentships so that there will be no financial burden on the Society. The aim is to award one and perhaps two or three studentships every year. Council hopes that members will wish to contribute to the Prize Fund. I commend this initiative of Council to all members.

I believe the Society should not be afraid to spend some of its limited financial reserves on marketing itself, selling its image and increasing its services to members. The Society should arrange e-mail facilities at its office sooner rather than later.

6.4 Meetings

I believe that the overall quality of the Society's Monthly Meetings needs to be improved. The 1999 Programme is an excellent Programme and the best the Society has had in recent years, due largely to the hard work of the incoming President. There may be a rationale for having a thematic character to the Monthly Meetings.

There is certainly no shortage of topics which would be of interest to our members. I mention 2 topics only:

Information Revolution and Electronic Commerce – these are changing society more rapidly than either the agricultural or industrial revolution.

Biological Revolution – to date, this has been used mostly in agriculture and crop production, but there are exciting possibilities and also downside risk in human genetic engineering and cloning.

I believe the Society ought hold half day or one day symposia once or twice a year. This reinforces the view stated by the President Sir Ronald Nyholm(21) in his 1955 Presidential Address when he referred to a Symposium on Oil organised by the Royal Society. He stated "I believe we have a responsibility to the community to hold more of these informative symposia on topics of current national interest."

6.5 Branches

The Society has two Branches – the Southern Highlands Branch and the New England Branch.

Regrettably, the New England Branch has been dormant for the last few years. Council should set in train procedures for its reactivation. If this is not possible, the Branch should be dissolved.

The Southern Highlands Branch is to be congratulated on the quality of its meetings and speakers, and the large attendance – upwards of 120 – at many of its meetings. This is a result of having a very active, dedicated committee, pro-active in its approach to selection of lecture topics, speakers and publicity. In many ways, Council would do well to emulate its sibling.

7. CONCLUSIONS

To conclude, I believe a 'Yes' vote at the November 1999 Referendum will not require a name change for the Royal Society of New South Wales. We should retain the term "Royal" in our name and should defend its retention. We should change name only if required by Government legislation. Historical perspectives are important and the name of the Royal Society of New South Wales does set us apart from other societies and groups operating in similar areas.

Also, I believe a 'Yes' vote will not immediately affect the status and *modus operandi* of our Society.

It is difficult to quantify any changes in the images that might be conveyed to and interpreted by the public by continued use of the title "Royal". Because fewer Australians have any kind of strong attachment to the monarchy, it seems inevitable that the title "Royal" will have less significance in future years.

The Society has played a useful and in its earlier years a significant role in the encouragement of studies in science, art and literature and in the promotion and development of science and the dissemination of scientific information.

Much has been done, but much more is yet to be done. Over time the scientific and social environment in which the Society operates has changed and the Society must also change. The Society should not be afraid to change and to engage more directly in public debate on scientific and social issues relevant to the community in which we live and work. This should be done in parallel with providing a higher standard of service to its members.

I take this opportunity to thank members of Council for the assistance and co-operation I have received throughout the year. I wish Professor Baker and the incoming Council every success in their endeavours.

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Metal Complexes of Linear Sexadentate Ligands: Dwyer and Lions Revisited

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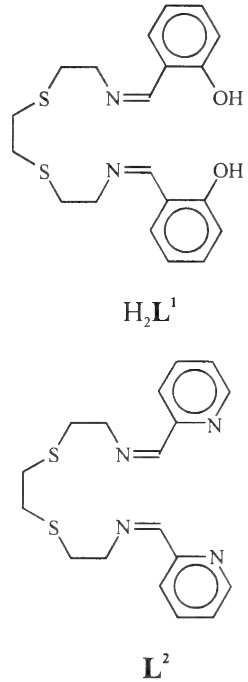
ABSTRACT: The linear sexadentate ligands 1,8-bis(salicylideneamino)-3,6-dithiaoctane ($H_2\mathbf{L}^1$) and 1,8-bis(2-pyridylmethyleneamino)-3,6-dithiaoctane ($\mathbf{L}^2$) have been prepared and a number of metal complexes have been isolated. The ligands have been characterised by nmr spectroscopy and mass spectrometry. The metal complexes have been characterised by electrospray mass spectrometry, electronic spectroscopy, microanalyses and magnetic susceptibility measurements. Three complexes have been structurally characterised by x-ray diffractometry (all triclinic, space group $P\bar{1}$, Z 2): $[Ni\mathbf{L}^2][ClO_4]_2$ a 9.963(4), b 10.953(5), c 13.145(5) Å, α 103.43(2), β 96.75(2) γ 116.06(2)°, R 0.038 for 3193 observed reflections; $[Fe\mathbf{L}^2][ClO_4]_2$ a 9.771(4), b 10.783(5), c 13.126(5) Å, α 104.07(2), β 96.81(3) γ 114.91(2)°, R 0.039 for 2364 observed reflections and $\{[CuH\mathbf{L}^1][ClO_4]\}_2.CH_3CN.0.5H_2O$ a 11.762(7), b 13.647(8), c 16.207(10) Å, α 82.41(4), β 79.98(4) γ 76.79(5)°, R 0.060 for 3977 observed reflections.

Keywords: sexadentate ligands, metal complexes, crystal structures.

INTRODUCTION

Both 1,8-bis(salicylideneamino)-3,6-dithiaoctane ($H_2\mathbf{L}^1$, Fig. 1) and 1,8-bis(2-pyridylmethyleneamino)-3,6-dithiaoctane ($\mathbf{L}^2$, Fig. 1) have been known for a considerable time. The molecules were both synthesised in the 1940s and 1950s by Dwyer and Lions and their co-workers, having been designed to act as sexadentate ligands able to provide all six donor atoms for binding to a metal ion preferring octahedral stereochemistry. $\mathbf{L}^2$ binds in its neutral form and $H_2\mathbf{L}^1$ was usually reacted in mildly basic conditions binding as the dianion ($\mathbf{L}^1$) on deprotonation of the hydroxyl groups. It was recognised that the metal complexes derived from these ligands would be chiral and metal complexes of $\mathbf{L}^1$ displayed the highest specific rotations observed to the time of their preparation (Dwyer and Lions, 1950).

In this work we have reprepared $H_2\mathbf{L}^1$ and $\mathbf{L}^2$ with a view to structurally characterising metal complexes of the ligands. Recently, there has been a great deal of activity in the general area of linear sexadentate ligands, principally those based on nitrogen heterocycles, because of the interesting



$H_2\mathbf{L}^1$

$\mathbf{L}^2$

Fig. 1. Ligands.

molecular topologies of metal complexes derived from such ligands (Constable, 1994). It is possible that some of the complexes originally isolated by Dwyer and Lions may not be mononuclear and have interesting structures. Given the methods available to them, there was no way of being absolutely certain of the molecularity of their complexes. Electronic spectroscopy and magnetic measurements have been used to further probe the electronic structure of the complexes. In the magnetic studies of the iron(II) complex of ligand $\mathbf{L}^1$, an unusual magnetic moment was reported, somewhere between the values expected for high-spin and low-spin octahedral iron(II) complexes (Dwyer, Lions and Mellor, 1950). The explanation offered in the paper is unsatisfactory, by present standards, and we have pursued further work on the iron(II) compound.

EXPERIMENTAL

Syntheses of ligands

1,8-Diamino-3,6-dithiaoctane

This compound was initially prepared by the literature method (Dwyer and Lions, 1950). The details of that preparation are not reported here. Identity of compounds and purity were determined by comparison of melting points with literature values, proton nmr spectroscopy and electrospray mass spectroscopy. The diamine was also prepared by a method adapted from the reported synthesis of 1,9-diamino-3,7-dithianonane (Hay, Gidney and Lawrance, 1975). The method is presented below.

2-Aminoethanethiol hydrochloride (13.50g, 0.12mol) was added, with stirring under nitrogen, to a solution of sodium ethoxide, prepared by dissolving sodium (5.08g, 0.22mol) in absolute ethanol (100ml). The mixture was heated under reflux and a solution of 1,2-dibromoethane (9.3g, 0.05mol) and sodium iodide (15g, 0.1mol) in absolute ethanol (200ml) was added dropwise. When the addition was complete (*ca.* 2h) the mixture was heated under reflux with stirring under nitrogen for a further 16h. After cooling and filtering the reaction mixture, the solvent was removed on a rotary evaporator. The residual oil was treated with water (10ml) and the mixture extracted with chloroform (6x20ml). The chloroform extracts were combined, dried over anhydrous sodium sulfate, and the chloroform removed on a rotary evaporator to give 1,8-diamino-3,6-dithiaoctane as a pale yellow oil, yield 5.8g (65%). The *diamine* was stored in a desiccator over sodium hydroxide pellets as amine rapidly absorbs water vapour and carbon dioxide from the air.

1,8-Bis(salicylideneamino)-3,6-dithiaoctane ($H_2\mathbf{L}^1$)

This compound was prepared by the literature method (Dwyer and Lions, 1950), m.p. 106° (literature 108°); ES mass spectrum: m/z 389.2 (M + H$^+$).

1,8-Bis(2-pyridylmethyleneamino)-3,6-dithiaoctane ($\mathbf{L}^2$)

This compound was prepared as described in the literature (Dwyer, Gill, Gyarfas and Lions, 1957), m.p. 58° (literature 59-60°); ES mass spectrum: m/z 359.2 (M + H$^+$).

Complex Syntheses

*(1,8-Bis(salicylideneaminato)-3,6-dithiaoctane)nickel(II) [Ni(**L**^{1})] and (1,8-Bis(salicylideneaminato)-3,6-dithiaoctane)copper(II) [Cu(**L**^{1})]*

These compounds were prepared by the literature method (Dwyer and Lions, 1950).

*(1,8-Bis-(salicylideneaminato)-3,6-dithiaoctane)iron(II) Dihydrate [Fe(**L**^{1})].2H_2O*

A solution of H_2**L**^{1} (0.50g, 1.3 mmol) in degassed methanol (10ml) was added to a solution of iron(II) acetate (0.25g, 1.3 mmol) in degassed hot methanol (10ml) under nitrogen. The red iron(II) complex formed immediately and precipitated on cooling. The complex was collected and recrystallized from hot benzene. Found: C 50.17, H 5.20, N 5.62 %; Calculated for $C_{20}H_{26}FeN_2O_4S_2$ ([Fe**L**^{1}].2H_2O): C 50.21, H 5.48, N 5.86 %

NOTE: All complexes of **L**^{2} have been isolated as **perchlorate** salts. Due caution should be exercised in handling these compounds as there is a risk of explosion.

*(1,8-Bis(2-pyridylmethyleneamino)-3,6-dithiaoctane)nickel(II) Perchlorate [Ni(**L**^{2})](ClO_4)$_2$*

A solution of nickel perchlorate hexahydrate (1.53g, 4.2 mmol) in methanol (15ml) at 40° was treated with a solution of the base **L**^{2} (1.50g, 4.2 mmol) in methanol (15ml). Fine reddish-purple solid separated. Red crystals were obtained by diffusion of diethyl ether into an acetonitrile solution.

*(1,8-Bis-(2-pyridylmethyleneamino)-3,6-dithiaoctane)iron(II) Perchlorate [Fe(**L**^{2})](ClO_4)$_2$*

A solution of **L**^{2} (0.5g, 1.4 mmol) in degassed methanol (10ml) was added to a solution of iron(II) perchlorate hexahydrate (0.51g, 1.4 mmol) in degassed hot methanol (10ml), under nitrogen. The red prepcipitate formed on cooling the reaction mixture The crude product was recrystallized by vapour diffusion of diethyl ether into an acetonitrile solution, forming very dark-red needles.

*(1,8-Bis(2-pyridylmethyleneamino)-3,6-dithiaoctane)copper(II) Perchlorate [Cu(**L**^{2})](ClO_4)$_2$*

A solution of **L**^{2} (0.2g, 0.6 mmol) in methanol (10ml) was added to a solution copper(II) perchlorate hexahydrate (0.21g, 0.6 mmol) in methanol (10ml). Fine green solid separated. The product was collected and recrystallized from acetonitrile upon diffusion of diethyl ether.

Mass Spectra

All electrospray mass spectra were measured using a Perkin-Elmer SCIEX API365 mass spectrometer with liquid chromatography accessories.

UV-Vis Spectroscopy

All spectra were measured using a Shimadzu UV2101PC spectrophotometer. Solid-state spectra were measured using an integrating sphere attachment. Solution spectra were recorded for approximately 3 x 10^{-2} M solutions.

Magnetic susceptibility measurements

Magnetic susceptibilities were measured using a Newport Gouy balance with a liquid nitrogen cooled cryostat. The magnetic balance was calibrated using $CoHg(NCS)_4$. All diamagnetic corrections were based on Pascal's constants.

Crystallography

Details for the three structure determinations, including information about the compounds, are given in Table 1. All data were collected using an Enraf-Nonius CAD4 diffractometer operating in θ/2θ scan mode. In all cases, graphite monochromatized MoK_α radiation (λ 0.71069 Å) was employed. The structures were solved by direct methods (Main, 1980) and refined by the method of least-squares (Rae, 1997). ORTEP-II (Johnson, 1976) was used for the structural diagrams including thermal ellipsoids.

Table 1. Crystal data, data collection, structure solution and refinement.

Formula	$[Ni\mathbf{L}^2][ClO_4]_2$	$[Fe\mathbf{L}^2][ClO_4]_2$	$\{[CuH\mathbf{L}^1][ClO_4]\}_2.CH_3CN.0.5H_2O$
Formula weight	616.1	613.3	1151.1
Space group	P$\bar{1}$ (No 2)	P$\bar{1}$ (No 2)	P$\bar{1}$(No 2)
a, å	9.963(4)	9.771(4)	11.762(7)
b, å	10.953(5)	10.783(5)	13.647(8)
c, å	13.145(5)	13.126(5)	16.207(10)
a, deg	103.43(2)	104.07(2)	82.41(4)
b, deg	96.75(2)	96.81(3)	79.98(4)
g, deg	116.06(2)	114.91(2)	76.79(5)
Cell volume (å^3)	1213.2(9)	1178(1)	2482(3)
Z	2	2	2
$2q_{max}$, deg	50	44	46
Reflections	4248	3065	6473
Refl with $I>3s(I)$	3193	2364	3977
Refined params.	283	282	407
R [SwD/SwF_o]	0.038	0.039	0.060
R_w [$(SwD^2/SwF_o^2)^{1/2}$]	0.058	0.055	0.075

RESULTS AND DISCUSSION

H_2**L**^{1} was prepared initially by the method described in the literature (Dwyer and Lions, 1950). This preparation involved refluxing the disodium salt of ethane-1,2-dithiol with 2-bromoethylphthalimide to yield 1,8-diphthalimido-3,6-dithiaoctane. The diamine, 1,8-diamino-3,6-dithiaoctane, was liberated by reaction with hydrazine hydrate in acid conditions and subsequent basification (Dwyer and Lions, 1950). The diamine, 1,8-diamino-3,6-dithiaoctane, has also been prepared by reacting the sodium salt of 2-aminoethanethiol with 1,2-dibromoethane in an adaptation of the method reported for the preparation of 1,9-diamino-3,7-dithianonane (Hay, Gidney and Lawrance, 1975). The diamino compound was then reacted with salicylaldehyde (2:1 mole ratio) to yield H_2**L**^{1}. Reaction of 1,8-diamino-3,6-dithiaoctane with pyridine-2-carbaldehyde (2 moles) was used to produce **L**^{2} (Dwyer, Gill, Gyarfas & Lions, 1957).

Metal complexes of **L**^{1} were produced by reacting a solution of a metal acetate with a solution of the ligand (H_2**L**^{1}), as previously reported (Dwyer and Lions, 1950). The iron(II) complex of **L**^{1} was analysed for C, H and N because of the interest in the magnetic properties. This analysis revealed the complex to be a dihydrate, whereas the original sample was anhydrous (Dwyer & Lions, 1950). In preparing a copper(II) complex of **L**^{1}, copper(II) perchlorate was inadvertently used on one occasion. It was possible to grow crystals of the copper(II) compound by diffusion of diethyl ether vapour into an acetonitrile solution of the complex. The complex was found (by crystal structure analysis) to have the formulation $\{[CuH\mathbf{L}^1][ClO_4]\}_2.CH_3CN.0.5H_2O$. The complexes of **L**^{2} were isolated as perchlorate salts through reaction of a solution of the ligand with a solution of the appropriate metal perchlorate.

All complexes were characterised by electrospray mass spectroscopy. The data are summarised in Table 2. All assignments are based on ^{58}Ni, ^{56}Fe, ^{63}Cu and the most common isotopes of the other elements. The pattern of abundances around the quoted peak was examined to confirm that ions were metal-containing or otherwise. In the mass spectrometer, the iron(II), nickel(II) and copper(II) complexes of **L**^{1} form cations through protonation of the neutral complexes. This indicates that the simplest means of ionising the neutral molecules [M**L**^{1}] are forming cations through adding protons. Clearly complexes of **L**^{2} can most simply form a monocation by forming an ion pair with the counterion, so $[M(\mathbf{L}^2)ClO_4]^+$ ions are present in the spectra and in the case of the copper(II) complex this ion is the base peak of the spectrum. Other ions noted in the mass spectra of the complexes of **L**^{2} include $[M\mathbf{L}^2]^+$ and $[H\mathbf{L}^2]^+$.

The field strength of ligands can be estimated by comparison of spectra of the nickel(II) complexes because the lowest energy transition (ν_1) corresponds to Δ_o in octahedral complexes. The solid-state reflectance spectra have been measured and the data are presented in Table 3.

Three electronic transitions are expected for octahedral nickel(II) complexes: $^3T_{2g}\leftarrow{}^3A_{2g}$ (ν_1), $^3T_{1g}\leftarrow{}^3A_{2g}$ (ν_2) and $^3T_{1g}(P)\leftarrow{}^3A_{2g}$ (ν_3), in order of energy. In the case of the complex of **L**^{1} two transitions are observed with the third being obscured by a charge-transfer band. In the spectrum of the nickel(II) complex of **L**^{2} the third band is obscured by a charge-transfer absorption and the second band appears as a shoulder on a charge-transfer band. A ratio of ν_2/ν_1 in the range 1.5 –1.6 is indicative of octahedral

Table 2. Significant ions (*m/z* values) in the electrospray mass spectra of the metal complexes

a) Complexes of **L**^{1}

Ion	[Fe(**L**^{1})]	[Ni(**L**^{1})]	[Cu(**L**^{1})]
[M(**L**^{1})] + H$^+$	443* (42)	445* (100)	450* (100)
[H$_2$**L**^{1}]$^+$ + H$^+$	389 (100)		389 (7)
Other		298* (18)	346* (24)

b) Complexes of **L**^{2}

Ion	[Fe(**L**^{2})](ClO$_4$)$_2$	[Ni(**L**^{2})](ClO$_4$)$_2$	[Cu(**L**^{2})](ClO$_4$)$_2$
[M(**L**^{2})ClO$_4$]$^+$	513* (10)	515* (24)	520*(100)
[M(**L**^{2})]$^+$	414* (7)		421* (7)
H**L**^{2}	359 (100)		
Other		283 (56) 223 (100)	

The percent abundance of the ion is shown in parentheses after *m/z* value. The asterisks indicate that, on the basis of the isotopic patterns, the ion contains metal.

Table 3. Solid-state electronic spectra for [Ni(ligand)]X$_2$

Ligand	Anion (X)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_2/ν_1
L^1	—	11 700	18 300	1.56
L^2	ClO$_4$	12 300	19 100 sh	1.55

geometry (Lever, 1984). The value of this ratio for both the nickel(II) complexes is in the middle of the expected range, confirming a close approximation to octahedral geometry. The value of Δ_o for **L**^{2} suggests that the iron(II) complex will be low-spin, as was observed. The value of Δ_o for the nickel(II) complex of **L**^{1} indicates that the ligand is of lower field strength than **L**^{2}. The value of Δ_o observed in the nickel(II) complex of **L**^{1} (11 700 cm^{-1}) suggests that the analogous iron(II) complex may undergo a thermally-induced spin-transition (Baker, Singh & Vignevich, 1991). A thermal equilibrium between the $^5T_{2g}$ and $^1A_{1g}$ states may explain the unusual room temperature magnetic moment previously

Table 4. Magnetic Data for [Fe(L^1)].$2H_2O$

Temperature (° K)	Molar Susceptibility (10^{-2} cgs units)	Magnetic Moment (BM)
303.7	1.16	5.30
275.0	1.27	5.29
244.9	1.39	5.21
200.8	1.65	5.15
156.6	2.07	5.10
127.6	2.41	4.96
102.6	2.89	4.87

observed for [Fe($\mathbf{L}^1$)] (Dwyer, Lions and Mellor, 1950). Variable-temperature magnetic susceptibility data were collected and it appears that [Fe($\mathbf{L}^1$)].$2H_2O$ is a simple paramagnet with a room temperature magnetic moment of 5.30 BM, normal for high-spin six-coordinate iron(II) complexes. It was noted that there is some decrease in effective magnetic moment at temperatures approaching the boiling point of liquid nitrogen (Table 4). This may be the sign of the onset of a spin-transition but this cannot be confirmed without further magnetic susceptibility data at lower temperatures.

Solid-state spectra of the copper(II) complexes have been measured. The spectra are relatively simple with a single broad band observed for each complex as expected for six-coordinate copper(II) complexes. Similar spectra have been observed for bis(tridentate ligand)copper(II) complexes (Lever, 1984). It is noted that for the spectrum of the copper(II) complex of $\mathbf{L}^1$ the absorption due to a d-d transition partially overlaps a charge-transfer band. The spectrum of the copper(II) complex of $\mathbf{L}^1$ has λ_{max} at 645 nm (15 500cm^{-1}) and the copper(II) complex of $\mathbf{L}^2$ has λ_{max} at 666 nm (15 000 cm^{-1}). These data appear to indicate that $\mathbf{L}^1$ has a greater ligand field strength than $\mathbf{L}^2$. However the position of λ_{max} does not give a direct measure of the ligand field strength because of the overlap of the charge-transfer band with the ligand field band. Another factor to be considered is that the copper(II) complexes display Jahn-Teller distortion and ligands will have differing capacities to accommodate the distortion.

X-ray crystallography has been employed to determine the structures of the isomorphic complexes [M$\mathbf{L}^2$][ClO_4]$_2$, where M = Fe and Ni. The cell parameters in Table 1 for these two complexes are very similar. Both complexes crystallise in the space group $P\bar{1}$ which means that both enantiomers are present in the crystals. The structure determinations confirm that the complexes crystallise as discrete anions and complex cations. The anions are present as counterions in the crystal lattice and there does not appear to be any interactions such as hydrogen-bonding between the anions and cations. The cation of the nickel complex is shown in Fig. 2 (the structure of the cation of the iron complex is essentially identical) and the metal – donor atom bond lengths are presented in Table 5.

Table 5 Metal – donor atom distances (Å) for [ML^2][ClO_4]$_2$

Bond	M = Ni	M = Fe
M-S1	2.438(1)	2.264(1)
M-S2	2.442(1)	2.265(1)
M-N1	2.097(3)	1.981(4)
M-N4	2.092(3)	1.982(4)
M-N2	2.020(3)	1.917(4)
M-N3	2.025(3)	1.916(4)

The cation is comprised of a metal centre and one molecule of $\mathbf{L}^2$ arranged to occupy all coordination sites for the six-coordinate metal ion.

The coordination sphere in both complex cations closely approximates octahedral geometry with the bond angles about the metal centre not deviating greatly from ideal values. The values that deviate furthest from 90° are the 'bite angles' associated with the planar chelate rings (N1-M-N2 and N3-M-N4) which are close to 80° in both complexes. The other chelate rings are more flexible and the bite angles are closer to 90°. The Ni-donor atom bond lengths are within one standard deviation of the average values obtained from analysis of parameters for many structures with chemically equivalent donors in the Cambridge Crystallographic Database (mean values quoted with estimated standard deviation in parentheses): Ni-S() 2.416(37) Å, Ni-N(pyridine) 2.122(42) Å and Ni-N(Schiff base) 2.051(34) Å (Orpen, A.G. *et al.*, 1989). It is interesting to note that the Ni-N bond lengths are significantly different and depend on the chemical environment of the donor atom. In the structure of [Ni$\mathbf{L}^2$][ClO_4]$_2$ the Ni-N bond lengths are slightly shorter than the average values quoted above whereas the Ni-S bonds are slightly longer than the average, suggesting that the planer chelate rings allow a closer approach of the donor atoms to the metal centre. The saturated chelate rings may have some slight strain hence the Ni-S bonds are marginally elongated.

In the iron(II) complex the metal – donor atom bond lengths are largely as expected. One interesting observation is that the Fe-N2 and Fe-N3 bond lengths are rather short in comparison to the averages obtained from analysis of the Cambridge Crystallographic Database at 1.958(21) Å. Perhaps related is the observation that the Fe-N1 and Fe-N4 bond lengths are greater than the average (1.961(12) Å) for pyridinyl donors in low-spin iron(II) structures. These deviations could be explained as a case of the tetragonal compression often observed in octahedral complexes of relatively rigid tridentate nitrogen heterocyclic ligands, such as 2,2':6',2"-terpyridine (Baker, Craig and Rae, 1995). The M – $N_{central}$ distance is often substantially shorter than the Fe-N_{distal} distance, the distortion presumably occurring so that all donor atoms can reach reasonable bonding sites. Ligand $\mathbf{L}^2$ can be interpreted as a sexadenate ligand comprised of two planar tridentate ligand fragments and in each fragment a 'long, short, long' pattern of metal -

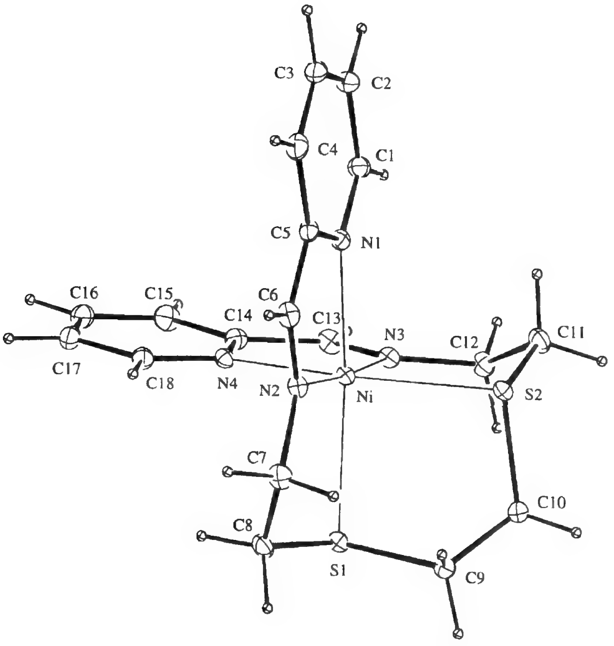


Fig. 2. An ORTEP representation of the [Ni**L**^{2}]$^{2+}$ cation.

donor atom bond lengths might be expected. However, it is noticed that the Fe-S bond lengths are slightly less than the average value (Fe-S(thioether) 2.301(28) Å) obtained from the Cambridge Crystallographic Database, the average does not take account of spin-state however, so comparison is difficult. In the nickel(II) complex, where different spin-states are not possible for octahedral complexes, there is no easily interpretable pattern: the Ni-S bonds are relatively long, being at the upper quartile value determined from many structures, the Ni-N(imine) bond lengths are slightly short, being close to the lower quartile value and the Ni-N(pyridine) bond lengths are also near the lower quartile value.

An important aim in this project was to structurally characterise a complex of the ligand **L**^{1}, preferably the iron(II) complex, since the structure may further illuminate the question of the magnetic behaviour of the complex. In attempting to grow crystals for x-ray studies the only complex that formed crystals of a quality suitable for x-ray diffraction was a copper(II) complex that had been prepared by reaction of a solution of copper(II) perchlorate with a solution of H_2**L**^{1}. Determination of the structure indicated that one perchlorate anion was present as a counterion for each metal complex, indicating that the complex was a cation. From spectroscopic data, it is clear that the oxidation state of the copper in the complex is +2. On the basis of the structure determination it is assumed that H_2**L**^{1} has been deprotonated in complex formation but has only lost one proton. The crystal structure determination has not revealed the location of the remaining proton. Inspection of final Fourier difference maps did not reveal the location

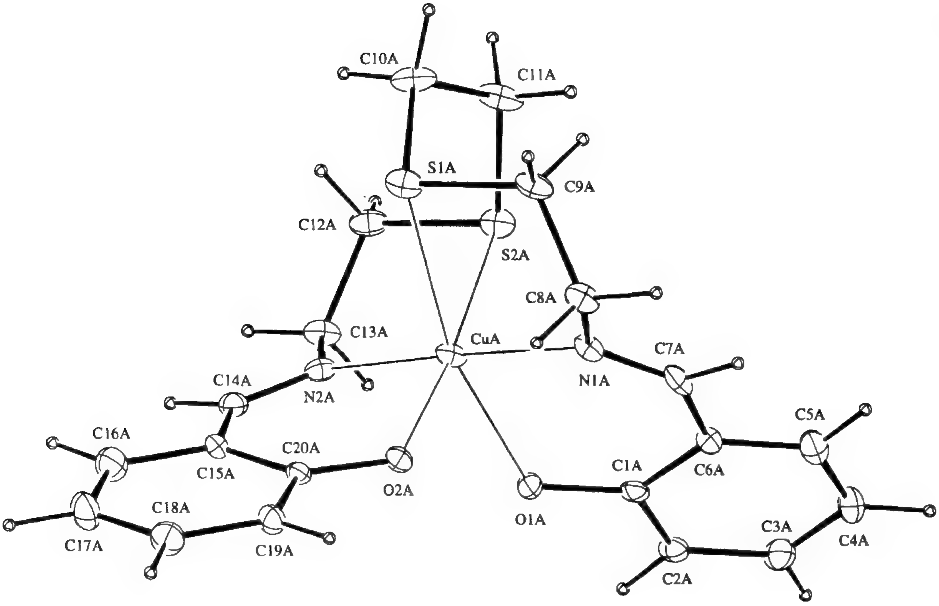


Fig. 3. An ORTEP representation of the $[Cu(H\mathbf{L}^1)]^+$ cation.

of the proton but it is speculated that the oxygen atom involved in the long Cu-O bond may be protonated. The crystals for the structure determination were grown by diffusion of diethyl ether vapour into an acetonitrile solution of the complex. The crystal used for the structure determination was probably not representative of the sample as the microanalysis figures cannot be interpreted in terms of the formulation $\{[CuH\mathbf{L}^1][ClO_4]\}_2.CH_3CN.0.5H_2O$, the stoichiometry determined through the crystal structure. It is noted that the figures also do not agree with the formulation $[Cu\mathbf{L}^1]$ either. The microanalytical data (C 35.12, H 4.31, N 5.59 %) indicate that there must be a substantial 'inorganic' fraction in the compound. It was found that the calculated values for $C_{22}H_{33}CuCl_2N_3O_{13}S_2$ (formulation $[Cu(H_2\mathbf{L}^1)][ClO_4]_2.CH_3CN.3H_2O$): C 35.41, H 4.45, N 5.63 % match the experimental data closely. A copper analysis was carried out (by AAS) and the result (Cu 8.4%) matches the percentage calculated for the proposed formulation above (Cu 8.51%). The recrystallised sample would appear to essentially be the complex formed between copper(II) perchlorate and $H_2\mathbf{L}^1$ without any deprotonation of the ligand.

There are two crystallographically independent cations in the asymmetric unit in space group $P\bar{1}$, which means, as in the case of the iron(II) and nickel(II) complexes of $\mathbf{L}^2$, that both enantiomers are present in equal populations. Packing diagrams were inspected and it was found that the anions and solvate molecules occupy well-defined volumes in the crystal lattice and do not have any significant interactions with the cations. The structure of one of the independent cations is shown in Fig. 3 and the copper – donor atom bond lengths are presented in Table 6. The structures of the independent cations are very similar, with the greatest differences observed relating to metal – donor atoms distances. The assumption that the metal centres are copper(II) is further supported by the observation of Jahn-Teller distortion in the structures of the complex cations. This

Table 6 Metal – donor atom distances (Å) for $\{[CuHL^1][ClO_4]\}_2.CH_3CN.0.5H_2O$

Bond	Cation A	Cation B
Cu-O1	2.262(5)	2.312(5)
Cu-N1	1.974(7)	1.982(7)
Cu-S1	2.648(3)	2.726(3)
Cu-S2	2.472(3)	2.410(3)
Cu-N2	1.949(7)	1.936(8)
Cu-O2	2.008(5)	1.978(5)

distortion will arise for 6-coordinate complexes of cations with d^9 electron configurations, because of the uneven occupation of the e_g orbitals but would not be observed for a complex with a d^{10} metal centre. The Cu – N distances are all similar, ranging between 1.936(8) and 1.982(7) Å, because in both cations these donor atoms are in the axial plane. The tetragonal elongation means that the Cu – O and Cu – S distances vary considerably, with the axial donors (S1 and O1) being considerably further from the metal centre than those in the equatorial plane (S2 and O2).

This work has confirmed that **L**^{1} and **L**^{2} are capable of binding as sexadentate ligands, forming mononuclear complexes. There is no evidence from electrospray mass spectrometry for formation of dinuclear complexes. The iron(II) complex of **L**^{1} appears to be a high-spin paramagnet at room temperature in contrast to the unusual intermediate magnetic moment previously reported (Dwyer, Lions and Mellor, 1950). Some caution is necessary in that our sample analysed as a dihydrate whereas the previously reported sample was anhydrous; it is known that the degree of hydration can significantly influence spin-state for iron(II) complexes near the spin crossover (Baker & Goodwin, 1977). Our studies suggest that the field strength of **L**^{1} is very close to the crossover for iron(II) and a study of the magnetic susceptibility over the temperature range 100-300 K suggests that some spin-pairing is occurring at the lower temperatures.

Further details of the three crystal structures reported (bond lengths, bond angles, atomic coordinates, thermal parameters) are available from the corresponding author or from the Cambridge Crystallographic Database.

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"...a small fish in a small pond...."
The Reverend W.B. Clarke (1798-1878): 200 Years On (Part II)*

Michael Organ

CRITICS

Over the years much had been written which is praiseworthy of Clarke, though in recent times more critical assessments have also appeared (Blainey, 1961; Branagan 1978; Vallance 1981). From the earliest days of his residence in Australia, Clarke came into conflict - and initiated conflict - with members of local society, largely as a result of his power and influence as a writer and commentator for the *Sydney Morning Herald*. Using anonymity as a protection against litigation, he could be scathing in his criticism of authority or individuals, stirring up debates on religion, education, science, and exploration. For example, he was a strong defender of the German explorer and scientist Ludwig Leichhardt, a stance which brought him into direct confrontation with the Colony's official explorer and Surveyor General Thomas Livingstone Mitchell (Webster, 1980). The 'intellectual barrenness of the Colony' was also a common theme of his tirades in the press (Organ, 1992).

The ability to give vent to his often petty opinions via virulent, intemperate articles in the Sydney newspapers caused some damage to Clarke's scientific reputation. William Sharp Macleay took him to task on a number of occasions, both publicly and privately, as a result of such outbursts. It could be said that his intemperance also hindered efforts to obtain government support in developing a geological survey for the Colony of New South Wales - this did not occur until the 1870s, some twenty years after the Victorian equivalent had been set up. When Samuel Stutchbury was appointed Colonial Geologist in 1851, Clarke published a number of critical articles in the *Sydney Morning Herald*. Stutchbury, on reading these, noted '...the bitter and disappointed feelings of the writer (Clarke) at his application for the appointment (of Colonial Geologist) not having been complied with' (Branagan, 1992). When Stutchbury left the Colony in 1855 he was not replaced, in part due to the feeling among local politicians that the Reverend Clarke could adequately serve as *de facto* Colonial Geologist, whilst mineralogical surveyors such as William Keene would cover specific areas such as coal mining, *in lieu* of an official Geological Survey establishment.

When Clarke claimed the 'scientific' discovery of gold in Australia, following Edmund Hammond Hargraves' discovery in 1851, numerous forces railed against him. It was an argument he ultimately lost, though in the fight he was able to bring to the attention of government and the public at large his services to science and claim as 'scientific' discoverer of gold and other assorted minerals (Anon., 1861). Clarke could be a manipulator of both people and the press. As Geoffrey Blainey pointed out in 1961, 'A man who twists the written record as often as Clarke twists it probably has a flexible memory' (Blainey, 1961). Blainey was here referring to that

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* Part I was published in vol. 131, pp. 101-112.

famous quote by Governor Gipps to the Reverend gentleman on being shown a specimen of gold on 9 April 1844: 'Put it away, Mr. Clarke, or we shall all have our throats cut!' Blainey argued that Clarke, 'with his patriarchal air and prehistoric profile', changed the actual quote over time to enhance his own case before the 1861 committee investigating his role in the gold discoveries.

In recent time Clarke's critics have become more common. The old New South Wales versus Victoria rivalry – which was reflected in Clarke's own battles with Frederick McCoy – is perhaps seen in Darragh's comment that 'Clarke's work has been much overrated by many writers, particularly after his death' (Darragh, 1977). With reference to geological mapping, Darragh was critical of his behaviour during the 1870s, suggesting that 'jealousy and possibly frustration' led him to forestall assisting the Victorian Robert Brough Smyth in a project to construct a geological map of Australia. This assessment is obviously close to the mark, and reinforced by Clarke's scathing criticism of Smyth's work in an anonymous *Sydney Morning Herald* article of 15 May 1874. However, in his defence, it should be pointed out that Clarke had been working on a detailed geological map of New South Wales for a number of years, and was unable to get any government funding or support to publish it. The lack of an official Geological Survey in New South Wales or widespread land survey program by the Surveyor General's Department during the 1850s, as in Victoria, was also a major hindrance. When the subject of issuing a continental geological map was raised by Smyth in the early 1870s, Clarke had real doubts about the practical worth of producing any such large scale map, especially when so little was known geographically and geologically of areas located away from coastal and settled areas. Clarke's failure to initially pass this work on to his Victorian colleagues is in many ways understandable, though not necessarily in the true spirit of scientific endeavour and collaboration. It appears that he was eventually forthcoming, as Smyth's map of 1875 includes much of what subsequently appeared in Clarke's 1880 geological map of New South Wales. The late Tom Vallance perhaps best summed up much of the recent criticism when he wrote:

> 'Clarke undoubtedly had a very high opinion of his own talents, and took every opportunity to advise anyone who would harken.. I find it impossible to go beyond regarding the man as a small fish in a small pond. What makes him interesting is that it was practically a one-fish pond.' (Vallance, 1990).

Branagan, in discussing Clarke's treatment of Stutchbury, observed: 'While Stutchbury was in Australia, Clarke felt that his position as spokesman on geological matters was threatened. Later, when Stutchbury had departed, we find Clarke acknowledging the value of Stutchbury's work' (Branagan, 1992). These criticisms point to obvious flaws in Clarke's character, though he remains an interesting subject for study.

ACCOLADES

Amongst the many criticisms, accolades exist in equal if not greater number. English geologist Joseph Beete Jukes, in an 1842 letter from Sydney to his sister Amelia in England, referred to Clarke as one of the many 'pleasant acquaintances' he had made whilst visiting the Colony (Browne, 1891). Though Clarke's eligibility for the title 'The Father of Australian Geology' remains open to debate, when we look back to his contemporaries we find commentators such as Prof. John Smith, then President of the Royal Society of New South Wales, in 1879 noting how Clarke's 'cheery voice [was] ever ready with a kindly greeting for his fellow members and friends.' Smith has no qualms in citing Clarke as 'the discoverer of gold in Australia', whilst in reference to the 4th edition of *Sedimentary Formations* he states that it is 'the most valuable portion of Mr. Clarke's labours, and represents in epitome the results of the work of his life' (Smith, 1879).

In presenting the Murchison Medal to Clarke in 1877, the president of the Geological Society of London commented on his 'remarkable services in the investigation of the older rocks of New South Wales, - services which have led to a correct knowledge of the succession of the formations in that country' (Anon., 1877). Even a recent critic such as Darragh recognised that Clarke was 'virtually the only active worker there [in New South Wales] between 1856 and 1873,' even though his presence is also cited as one of the reasons for the failure of the New South Wales government to set up a geological survey during the 1850s.

During his lifetime Clarke led a busy public life, and received numerous honours as it drew to an end. Most notably, he was one-time Secretary and long-time Trustee of the Australian Museum, Trustee of the Free Public Library, Sydney (later State Library of New South Wales), and a Fellow of St. Paul's College, University of Sydney. He was offered a seat on the first University Senate in 1850, along with a Chair in Mineralogy and Geology during August 1853 - both of which he turned down due to his commitment to clerical duties and objections from the local Archbishop. He was a founding member and staunch supporter of the Australian Philosophical Society, which became the Philosophical Society of New South Wales and later Royal Society of New South Wales. He was a member of the Geological Society of France, the Geological Society of London (receiving its Murchison Medal in 1877), the Royal Geographical Society, the Royal Geological Institute of Austria, the Royal Society of London (elected a Fellow in 1876), the Royal Society of Literature, and the Zoological Society of London. Clarke served as a member of the New South Wales Commission for the Paris Exhibition of 1867, the Intercolonial Exhibition of 1870, and the Philadelphia Exhibition of 1877.

It can be seen from the above that Clarke was a 'persevering geologist' (Murchison, 1862) and 'indefatigable pioneer of civilisation and science' (de Koninck, 1898) who played a significant role in the correlation of the Australasian formations with those of Europe and the rest of the world during the nineteenth century. His major accomplishments locally were in delineating the geological timetable of eastern Australia over a period of some forty years from 1839-78, through palaeontological and stratigraphic investigations, and in acting as a promoter of past and ongoing discoveries in the fields of the natural and earth sciences. Primarily a scientist, his various mineral discoveries were ancillary to his ongoing work. He was no entrepreneur, and saw no need to exploit them, though he did seek recognition and acknowledgment of the role he played in assisting miners. Clarke worked systematically on providing a chronology of the earth history of eastern Australia, slowly developing the basic stratigraphy so that at the end of the day a geological map of the Colony could be published, based on biostratigraphic knowledge. If, after some 120 years, his reputation as a scientist is somewhat tarnished, Clarke nevertheless remains an interesting historical figure. Vallance's 'little fish in a little pond' epitaph may be too harsh an assessment of the man; perhaps 'big fish in a big pond' would be more fitting.

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Geology and Mineralogy of the Lorena Gold Mine, Cloncurry District, North-west Queensland

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Abstract. The Lorena gold deposit, near Cloncurry, northwest Queensland, contains an unusual Au-Bi-As-Cu-Co assemblage. Gold is intimately associated with native bismuth and bismuthinite, and the Co is confined to solid solution in arsenopyrite. Analyses of the primary phases and mineral associations point to a hydrothermal origin for the deposit. Secondary cobalt species include cobaltian conichalcite, heterogenite-2H, cobaltian calcite and abundant wupatkiite, the cobalt member of the halotrichite group. The major secondary enriched copper sulfide in the deposit is the rare species, geerite.

INTRODUCTION

The Lorena gold mine is located in the Mt Isa Block, northwest Queensland (54 414635E 7777709N), approximately 10 km east of Cloncurry (Fig. 1). The area surrounding the mine is known as the Pumpkin Gully field and is famous for its gold production, mostly during the latter stages of the last century (Jack, 1898; Ball, 1908; Carter *et al.*, 1961). Much of the gold won from the field was alluvial, although small hard rock trials, prospects and mines dot the region. Many of these were developed on small copper lodes, none of which produced more than a few tonnes of concentrates.

The Lorena deposit was discovered in the early 1980s by a prospector, Neil Lucas. Situated on a low ridge between Pumpkin Gully and Fisher Creek, it was overlooked by the early prospectors, although it is apparent that it must have been the source of a considerable amount of alluvial gold in the area, and it makes a distinct outcrop.

The mineralogy of the deposit was examined as part of a wider programme concerned with the geochemistry of cobalt and gold deposits in the Mt Isa Block. The mine is the second known locality of the rare cobalt mineral wupatkiite, a member of the halotrichite group. Geerite, an unusual supergene copper sulfide, is common as an alteration product of arsenopyrite. Rich gold mineralisation in the deposit is associated with cobaltian arsenopyrite, bismuthinite and native bismuth.

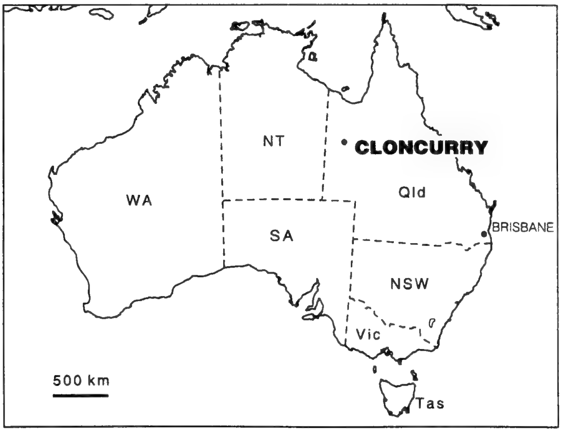

Fig. 1. Locality Map - Cloncurry

GEOLOGY

The deposit is situated in the Toole Creek Volcanics (being part of the Proterozoic Soldiers Cap Group), near the boundary of

TABLE 1. Primary and secondary ore minerals of the Lorena deposit.

A. Primary Minerals			
arsenopyrite	FeAsS	chalcopyrite	$CuFeS_2$
bismuth	Bi	gold	Au
bismuthinite	Bi_2S_3	pyrite	FeS_2
B. Secondary minerals			
azurite	$Cu_3(CO_3)_2(OH)_2$	halotrichite	$FeAl_2(SO_4)_4.22H_2O$
chalcocite	Cu_2S	wupatkiite	$CoAl_2(SO_4)_4.22H_2O$
chrysocolla	*ca* $CuSiO_3.nH_2O$	heterogenite-*2H*	CoOOH
conichalcite	$CaCuAsO_4(OH)$	libethenite	$Cu_2PO_4(OH)$
copper	Cu	malachite	$Cu_2CO_3(OH)_2$
covellite	CuS	olivenite	$Cu_2AsO_4(OH)$
cuprite	Cu_2O	pseudomalachite	$Cu_5(PO_4)_2(OH)_4$
goethite	FeOOH	scorodite	$FeAsO_4.2H_2O$
geerite	Cu_8S_5	hematite	Fe_2O_3

two units, amphibolite, metabasalt and metadolorite with minor metasediments and quartzite, phyllite, metamorphosed chert and siltstone, with minor meta-basalts. A fault hosts the deposit but is not marked on the 1:100 000 geological series map. The Naraku Granite is exposed less than 1 km south–east of the mine and is probably the source of mineralisation.

The Lorena gold deposit consists of a 20 m deep east-west pit approximately 130 m long, developed on a subvertical shear trending approximately 267°M. Confined to the contact or very near to the contact between laminated graphitic slates and schists and an altered basalt, the shear zone reaches a width of some 12 m. The main lode, from the surface to the base of the pit, in some sections, consists of gouge breccia cemented by quartz. The breccia fragments are either clasts of the sedimentary unit or thoroughly oxidised gossan blocks after sulfides. Towards the centre of the current pit, a subsidiary, earlier fault strikes 338°M and dips about 85° N. Approximately 30 m to the east, a second, parallel fault intersects the main shear zone. Both of these faults have been filled with highly siliceous vein material carrying abundant sulfides, principally pyrite and arsenopyrite, which are preserved near the surface due to intense silicification. Some alteration is however observed (see below). Gold values closely follow the arsenopyrite concentration, which is not, however, continuous throughout the shear system. Quartz-sulfide pods are seen to pinch and swell; coarsely crystalline calcite fills sections of the fault system.

TABLE 2. Primary mineral analyses.

	1	2	3	4	5	6	7	8	9	10
As	45.1	46.01	42.3	<0.1		<0.1		<0.1	<0.1	
S	19.7	19.69	21.6	53.5	53.45	34.6	34.94	22.8	24.6	23.98
Fe	32.1	34.30	33.5	45.2	46.55	28.9	30.43	0.6	0.2	
Co	1.3		0.1	<0.1		<0.1		<0.1	<0.1	
Ni	0.1		<0.1	<0.1		<0.1		<0.1	<0.1	
Cu	0.1		<0.1	0.4		33.4	34.63	75.0	73.5	76.02
Total	98.3	100.00	97.5	99.1	100.00	96.9	100.00	98.4	98.3	100.00

1: disseminated arsenopyrite, average of 2 analyses; 2: calc. for FeAsS; 3: massive arsenopyrite, average of 2 analyses; 4: pyrite, average of 4 analyses; 5: calc. for FeS_2; 6: chalcopyrite, average of 2 analyses; 7: calc. for $CuFeS_2$. Low analyses are attributed to altered and pitted mineral surfaces; 8: geerite, main lode, average of five analyses; 9: geerite, intersection of mainlode and cross-fault, average of five analyses; 10: calc. for Cu_8S_5.

EXPERIMENTAL

Polished sections of primary and secondary mineralisation initially were inspected by reflected light microscopy. Samples were then carbon coated and analysed using a JEOL JXA-8600 electron microprobe, controlled by JEOL software, with a beam current of 20 nA. Three wavelength dispersive spectrometers and an energy dispersive spectrometer controlled by Moran Scientific software were employed for the analyses, which were calibrated against kaersutite, marcasite and pure metal standards. X-ray powder diffraction measurements were carried out with a Philips PW1925-20 powder diffractometer using CuKα radiation. Microanalyses of wupatkiite were performed by G&M Laboratories Sydney, on hand-picked samples, subsequently dissolved in aqueous HNO_3, using ICP methods.

PRIMARY MINERALOGY

A list of minerals identified in the deposit is given in Table 1. The primary sulfide mineralogy of the Lorena Gold Mine consists principally of euhedral arsenopyrite, pyrite and chalcopyrite, mostly in a quartz matrix. Albite is common, as is calcite. Other notable primary accessory phases are xenotime, rutile and monazite. Graphite is common in the metasediments adjacent to the lode. Pyrite appears to have been deposited early. It was subsequently fractured and the fractures filled with arsenopyrite. Masses of arsenopyrite also show fracturing, with the fractures invaded by secondary phases. Two generations of arsenopyrite are recognised. Massive material contains negligible Co (Table 2) in solid solution; disseminated euhedral crystals are strongly cobaltian (Table 2). No Co was detected in the pyrite (Table 2), and no cobaltite, alloclasite or glaucodot was found in the samples examined. Analyses of drill core samples show no significant correlation between Co and As, due to the erratic distribution of the two generations of arsenopyrite. This is in contrast to other deposits containing both Co and As in the Mt Isa Block (Croxford, 1974). Chalcopyrite analysed by microprobe (Table 2) is near to ideal stoichiometry.

Gold is present as an anastomising network of microveinlets, blebs and masses in quartz ranging from 1 µm to matchhead size. It is invariably accompanied by veinlets and patches of bismuthinite and, more rarely, native bismuth, up to 20 µm across. The association of gold and bismuth has long been recognised in alluvials in Pumpkin Gully (Jack, 1898; Lindon, 1887). Analyses of gold associated with bismuth in primary ore show that it is very pure, containing only traces of Ag (Au, 99.1; Ag, 0.4; Fe, 0.9; Total, 100.4%).

In terms of geochemical relationships, the association of Au and Co parallels deposits and prospects in the southern section of the Mt Isa Block, in the Selwyn region. The bismuth association recalls similar geochemical settings at Top Camp (Jack, 1898; Lindon, 1887) at Soldiers Cap (Carter *et al.*, 1961) and in the Alone Hand mine, a small gold-bismuth-copper-tungsten deposit near Duck Creek, south of Cloncurry (Lawrence *et al.*, 1998). As suggested by Wyborn (1998), the mineralogical evidence is consistent with hydrothermal activity associated with the Naraku Granite, a part of which is exposed immediately to the south of the Lorena mine. Finally, in this connection, it is noted that the temperature of formation of the cobaltian arsenopyrite, derived from the ternary NiAsS - CoAsS - FeAsS relationships (Klemm, 1965) is about 300°C. Further work is required to clarify this point, since the FeAsS geothermometer, for the Co- free arsenopyrite (Clark, 1960; Kerestedjian, 1997; Kretschmar and Scott, 1976) gives an indicative temperature of formation of the primary mineralisation of about 200°C.

SECONDARY MINERALOGY

Table 1 lists the secondary metallic phases identified in the deposit. All of the material sampled is altered to some extent. Siliceous gold-bismuth-arsenopyrite ore is liberally coated on fractures and in cavities by scorodite. The freshest material obtained was greenish by virtue of the presence of this ubiquitous alteration product of arsenopyrite.

Supergene copper sulfides

Supergene enriched copper minerals are present, replacing pyrite, arsenopyrite and chalcopyrite along fractures. Covellite and the rare phase geerite (Anthony *et al.*, 1990) are the principal replacement products of chalcopyrite and arsenopyrite. Only minor chalcocite was observed replacing pyrite and chalcopyrite. Our identification of geerite is based on analysis; the replacement veinlets along fractures in the primary minerals are too small to permit recovery of sufficient material for X-ray analysis. This is the first reported Australian occurrence of geerite. It has been reported from four other localities to our knowledge and was associated with another very rare secondary copper sulfide, spionkopite, Cu_{39},S_{28}, in three of them (Anthony *et al.*, 1990; Sikka *et al.*, 1991). We have not analysed material with that composition, however, from the Lorena deposit.

TABLE 3. X-ray data for halotrichite and wupatkiite.

halotrichite JCPDS 39-1387		wupatkiite (Williams & Cesbron, 1995)		wupatkiite (this study)	
d/Å	Irel	d/Å	Irel	d/Å	Irel
15.8	20	15.8	8	15.7	10
12.1	8	12.2	1		
10.46	16	10.43	7	10.38	7
9.58	18	9.57	10		
7.91	15	7.90	10	7.88	12
		7.56	5		
6.71	2	6.70	1		
		6.40	7	6.37	8
6.02	35	6.03	22	6.03	28
5.91	2				
5.82	9	5.82	1		
5.68	1	5.71	1		
5.46	2				
				5.45	4
				5.29	5
5.27	7	5.27	11	5.26	9
5.11	1	5.09	5		
4.930	21	4.947	13	4.937	8
4.860	11				
4.780	100	4.790	100	4.789	95
4.660	10	4.660	10		
4.580	12	4.586	12	4.584	5
4.540	3	4.536	<1		
4.380	10	4.384	14	4.382	24
		4.366	2		
4.290	31	4.295	27	4.292	17
4.160	14	4.159	17	4.159	9
4.090	20	4.106	22	4.106	11
				4.018	10
3.987	12	3.980	14		
3.947	21	3.945	26	3.946	24
3.876	5	3.885	8		
3.751	27	3.768	33	3.766	32
3.705	2				
3.659	2	3.657	8	3.655	5
3.610	6	3.608	9	3.493	100
3.442	10	3.441	15	3.444	13
3.343	5	3.345	12	3.347	9
		3.322	8	3.323	5
3.285	7	3.289	6		
		3.272	8	3.271	6
3.252	6				
3.239	2	3.205	7		
3.199	2				
3.172	2	3.168	6	3.186	26
3.112	5	3.101	5		
3.062	8	3.072	1		
3.037	5	3.043	9	3.042	6
3.021	3	3.018	9	3.020	5
2.964	10	2.962	12	2.963	10
				2.918	5
2.889	11	2.887	13	2.889	10
		2.858	<1		
2.820	8	2.826	12	2.829	10
2.779	6	2.779	11	2.779	10
2.751	3	2.763	6	2.759	3
2.715	3	2.715	6	2.717	4
2.677	13	2.679	13	2.676	13
2.643	1	2.634	7		
2.611	10	2.607	9	2.608	9
		plus 29 extra lines to 1.858		plus 19 extra lines to 1.860	

Secondary copper minerals

Copper grades are low in the Lorena deposit. Although Table1 lists a number of secondary copper minerals, most of them are present in negligible amounts. The sole abundant secondary copper mineral observed is conichalcite. It is found as isolated crystals, rosettes of slender prisms and botryoidal crusts throughout the gossan breccia of the main shear zone, sometimes accompanied by pseudomalachite coatings and sprays of acicular olivenite crystals. Analyses of the conichalcite indicate that it contains small, but detectable, amounts of Co (up to 0.2%). Nowhere, however, does it approach the composition of cobaltaustinite, $CaCoAsO_4(OH)$.

Wupatkiite

Perhaps surprisingly, given the geochemistry of the Lorena deposit, erythrite has not been observed in the oxidised zone. Supposed erythrite ("cobalt bloom") was present in the two minor faults that intersect the main shear zone. Indeed, abundant pink needles encrust oxidizing primary ores at these sites. However, analysis of the pink material indicates that it is wupatkiite, the Co-dominant member of the halotrichite group (Williams and Cesbron, 1995). The identity of the mineral has been confirmed by powder X-ray diffraction and analysis. A list of X-ray data is given in Table 3.

Both samples, on dissolution in 10^{-2} M aqueous HNO_3 proved to contain rock chips which were not obviously present in the hand-picked material. Thus formulae are derived on the following basis. Ideally, the halotrichite member has the general formula $AB_2(SO_4)_4.22H_2O$ where $A = Fe^{2+}$ (halotrichite), Mg^{2+} (pickeringite), Co^{2+} (wupatkiite), Ni^{2+} (not reported as a mineral), Mn^{2+} (apjohnite), Zn^{2+} (dietrichite) and $B = Al^{3+}$, or $A = Fe^{2+}$ and $B = Fe^{3+}$ (bilinite) or Cr^{3+} (redingtonite). Analyses by ICP carried out by G & M Laboratories gave, after deducting 2.5 and 9.1 wt%, respectively, for insoluble material, Al, 5.19, 5.11; Co, 3.08, 2.67; Fe, 4.23, 4.00; Mg, 0.19, 0.42; Mn, 0.12, 0.24; Ni, 0.23, 0.40%, for the two hand-picked samples, respectively. Negligible amounts of Zn and Cr were present in the samples. Analyses were converted to a mol basis and normalised to 100%. Since the $A : B$ ratio is 1 : 2 and iron is distributed between the two sites, simultaneous solution of the following two equations gives unique values for all constituents for ideal stoichiometry.

$$2(N_{Fe^{2+}} + N_{Mg^{2+}} + N_{Co^{2+}} + N_{Ni^{2+}} + N_{Mn^{2+}}) = (N_{Fe^{3+}} + N_{Al^{3+}}) \tag{1}$$

$$N_{Fe^{2+}} + N_{Fe^{3+}} = N_{(Fe,\ total)} \tag{2}$$

Although Fe^{2+} does substitute to significant amounts in the A site for the samples analysed, Co^{2+} is the predominant A site cation in both cases. Derived formulae are $(Co_{0.469}Fe_{0.407}Mg_{0.070}Ni_{0.035}Mn_{0.019})(Al_{1.727}Fe_{0.273})(SO_4)_4.22H_2O$

and

$(Co_{0.406}Fe_{0.338}Mg_{0.156}Ni_{0.061}Mn_{0.039})(Al_{1.697}Fe_{0.303})(SO_4)_4.22H_2O$.

This is only the second reported occurrence of wupatkiite. At the Lorena, it is abundant and is present most likely because of the very acid conditions apparent for the oxidation zone of the deposit. In addition, while it is inevitably ephemeral on surfaces of exposed lode material, it is a natural alteration product as it was detected *in situ* in material collected immediately after exposure of the second fault zone by mining. Similar acicular material, but of a pale buff colour, in association with the wupatkiite proved to be the common phase halotrichite. Some heterogenite-*2H* and cobaltian calcite is present in the lodes where wupatkiite was found.

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Thesis Abstract: The Pathogenesis and Behaviour of Clinical Endocrinopathy in Multiple Endocrine Neoplasia Type 1

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Abstract of a Thesis Submitted for the Degree of Doctor of Medicine
at the University of Tasmania

Multiple endocrine neoplasia type 1 (MEN 1) is an autosomal dominant tumour syndrome characterised by poly-glandular parathyroid hyperplasia, pancreatic tumours and anterior pituitary neoplasia. The MEN 1 gene is believed to be a tumour suppressor gene and has recently been cloned. Genotype-phenotype correlations have not been identified thus far. This thesis sought to identify factors predicting the development and behaviour of endocrine tumours in patients with MEN 1. The patients studied derive predominantly from a large, multi-generational Tasmanian MEN 1 family (designated Tasman 1), of whom over 160 members carry a mutation of the MEN 1 gene. The prevalence, distribution and behaviour of pituitary disease, enteropancreatic neoplasia, adrenal tumours and parathyroid neoplasia has been examined. Acromegaly is often been cited as a cardinal pituitary manifestations of MEN 1. There is a complete and unexpected absence of acromegaly in the Tasman 1 family, suggesting that either the expression of acromegaly in Tasman 1 is attenuated or that the previously reported high prevalence of acromegaly in other MEN 1 families is the result of inadvertent inclusion of patients with MEN 1 phenocopy. Both factors appear contributory, as correlation of genetic and clinical screening data indicates conventional phenotypic criteria for MEN 1 diagnosis over-estimate the prevalence of genotypic MEN 1. The distribution of prolactinoma and enteropancreatic malignancy in the Tasman 1 family also suggests the involvement of genetic modifier factors in MEN 1 tumour pathogenesis. These tumour species occur frequently in some branches of the Tasman 1 family, whilst they are relatively uncommon in other parts of the kindred. Given common ancestry of the MEN 1 disease allele in Tasman 1, disease clustering cannot be explained by MEN 1 allelic heterogeneity. These observations suggest that additional genetic loci inherited separately from the primary MEN 1 locus have an important role in modulating tumorigenesis. Adrenal tumours in MEN 1 appear to develop in response to circulating growth factor(s) secreted by enteropancreatic tumours. Moreover, a propensity for parathyroid hyperplasia to recur despite extensive surgical resection of parathyroid tissue suggests a role for circulating growth stimuli in MEN 1 tumorigenesis.

In conclusion, this thesis shows that MEN 1 gene expression is modified by a variety of genetic and biological factors. The findings have implications for patient management as well as providing an insight into the mechanisms of tumour pathogenesis.

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Thesis Abstract: Conventional and Topographic Electroencephalography and Somatosensory Evoked Potential Studies in Ischaemic Stroke

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Abstract of a Thesis Submitted for the Degree of Doctor Of Philosophy

The purpose of this prospective study was to assess the diagnostic and prognostic value of early electroencephalography (EEG) and somatosensory evoked potential (SEP) studies in cortical and non-cortical ischaemic stroke. Both conventional and topographic/quantitative studies were performed. A parallel study was carried out on healthy volunteers to provide an effective control. Equipment and quantitative EEG (qEEG) variability was also assessed.

Equipment was tested using an external calibration source, from which some amplitudes fell outside the ±4% specified machine limits; a customised software upgrade rectified the problem. Voltage mapping showed that a single colour change could represent a variation of 1% to 25%. Intra- and inter-operator and inter-session qEEG studies showed that most variability occurred in Absolute Power, but no significant difference was detected between 3 operators.

Fifty-one unselected acute ischaemic stroke patients were assessed clinically. All underwent non-contrast computerised tomography (CT), 16-channel EEG, 21-channel topographic qEEG, 3-channel SEP and 21-channel topographic SEP studies within 48 hours of the stroke; forty-five underwent all tests 4 to 15 days later. Final stroke classification was based on full clinical assessment, including the later CT. Clinimetric assessment included an early and 3 month Barthel Index (BI). Sixty-five healthy volunteers underwent the above electro-physiological studies after a clinical assessment; fifty-one were studied 5 to 16 days later.

Seventy-three percent of the patients were considered to have had unilateral cortical stroke and logistic regression showed that the tests most discriminating between cortical and non-cortical stroke were qEEG and CT in the first session and qEEG in the second session, at the 0.05 level. Conventional and topographic SEPs were independently associated with BI outcome in the first session, while for the second session this association applied only to conventional SEPs. Models were developed that were predictive of group (cortical/non-cortical) and outcome.

In conclusion, topographic qEEG, reflecting altered brain function after stroke, was useful in distinguishing between cortical and non-cortical ischaemic stroke, while conventional and topographic SEPs proved useful indicators of functional outcome.

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Thesis Abstract: Capillary Zone Electrophoresis
Studies on Separation Selectivity of Inorganic Anions

ANTHONY H. HARAKUWE

Abstract of a Thesis Submitted for the Degree of Doctor of Philosophy
at the University of Tasmania

Parameters influencing the separation selectivity of low molecular-mass anions using free-solution reversed electroosmotic flow capillary zone electrophoresis (CZE) have been studied. First, detailed preliminary investigations were performed to address two major limitations of CZE, namely, imprecision in migration times and variability of phosphate response. A capillary conditioning regime suitable for the generation of stable migration times and optimal phosphate response was developed. Also, it was established that dried quaternary ammonium electroosmotic flow (EOF) modifiers generated more stable migration times and gave improved resolution.

Second, a wide range of selectivity-influencing parameters was studied. These parameters included electrolyte pH, EOF modifier chain length, nature of the EOF modifier counter-anion, EOF modifier concentration, binary EOF modifier mixtures, type of indirect detection probe, probe concentration, 1-butanol as an electrolyte additive, and instrumental variables (e.g. detection wavelength and separation voltage). The trends of migration order observed with the above parameters are discussed and possible mechanisms outlined. Major migration order changes were caused by pH and EOF modifier effects. Electrolyte pH variation changed the migration order of weak acid anions at pH values close to their pK_a points by altering their charge-to-mass ratios. Migration order changes due to either increased or reduced ion-pairing effects were pronounced for lipophilic anions and could be induced particularly with EOF modifier changes, electrolyte concentration and 1-butanol as additive. Migration order changes due to increased effective charge of anions were influenced particularly by pH, 1-butanol as additive, and electrolyte ionic strength.

Third, information from the above studies was applied to the separation of inorganic anions in samples having varying levels of matrix complexity, e.g. tap water, Bayer liquor, seawater, acid- digested concrete, toothpaste, urine, a formulation for prevention of gall-stone formation, corned beef, and Antarctic saline lake water. Analytical performance characteristics are discussed for the separation of anions in Bayer liquor, concrete, and toothpaste.

The highlights of this study were that the useful pH range of chromate-based electrolytes could be extended by 20% by incorporation of 1-butanol in the electrolyte; the resolution between fluoride and phosphate could be improved by over 400% making possible the separation of 1 $\mu g.mL^{-1}$ fluoride in the presence of over 800 $\mu g.mL^{-1}$ phosphate, and the use of binary EOF modifier mixtures was introduced and applied to the analysis of Bayer liquor. Two electrolyte compositions capable of simultaneously separating chloride, sulfate, oxalate, malonate, fluoride, formate, phosphate, succinate, tartrate, carbonate, and acetate in under 4 minutes were identified. Calibrations were linear in the range 1–10 µg.mL^{-1}, detection limits as low as 0.09 µg.mL^{-1} were obtained, and near quantitative recoveries (except for phosphate) were recorded.

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Thesis Abstract: The Management of Regional Economic Development Organisations with a Particular Emphasis on Funder Relationships

HELEN MONKS

Abstract of Thesis for the Degree of Doctor of Philosophy
at the University of New England, Armidale

The study aims to assist understanding of the management and organizational behaviour of regional development organisations in non-metropolitan Australia. The objective is to find new methodologies for studying regional development. The study will increase stakeholders' knowledge of appropriate management techniques.

This study has been undertaken when Australia is experiencing rural/urban and rural/coastal population movements exacerbated by difficult economic conditions in inland areas.

Maintenance of the economy in rural communities is the background to this work.

The theoretical context adopted for the study proposes that development organisations are entities operating within an environment which exercises political economic and social demands (an open systems view). However, the open system is modified here by the addition of permeable organisational boundaries.

The style of the thesis is empirical and multi-disciplinary rather than theoretical. Disciplines such as government, non-profit sector management, regional economic development and organisation theory contribute metaconcepts and diverse perspectives. A modified case study method is applied to two organisations in New South Wales, one government-owned and one community-based non-profit. A new analytical tool compares the impacts of five critical incidents upon each organisation, by their effect and source.

A comparison of summarised case study information suggests that organisational behaviour during the critical incidents differed distinctly. Specifically the non-profit organisation appeared to be more evenly: balanced than the government organisation in the quantity of its dealings with all stakeholders. Qualitatively, the former also had more positive transactions overall. Further, the government organisation appeared to have more negative transactions in total than the non-profit.

Strategic management of permeable organisational boundaries and of external relationships is proposed as being significant for organisational independence and viability. Five management factors are proposed as a framework for balanced proactive management. Finally, the study canvasses possible productive roles for stakeholders in their support of regional development organisations.

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Thesis abstract: A Study Of The Scaling Behavior Of Some Cr_2O_3 Forming Alloys With Relevance To Interconnect Plates For Solid Oxide Fuel Cells

FIROOZEH RABBANI

Abstract of a Thesis submitted for the Degree of Doctor of Philosophy
at the University of South Australia

Corrosion of metallic parts in low partial pressures of oxygen occur in oil and coal gasification processes, high temperature gas cooled reactor (HTGR) systems, fuel cells and fluidized bed combustion environments. However, there has been a lack of systematic work comparing/contrasting oxidation in air (high partial pressures of oxygen, high pO_2) and at low pO_2.

In this thesis the scaling behavior of some chromia forming alloys that had been used as metallic interconnects or current collectors for Solid Oxide Fuel Cells (SOFC) have been investigated. The oxidation behaviour of three 'superalloys', five laboratory cast nickel-chromium binary alloys, and pure chromium was assessed in air and low partial pressures of oxygen simulating on a small scale the environments encountered at the anode and cathode of a SOFC. Initially, two partial pressures of oxygen were studied using air and a hydrogen/water mixture thereby excluding the effects of carbon and sulfur. The emphasis in this study was on the differences that arose as a result of changes in the pO_2 and alloy composition, in particular chromium content. In air, nitrided layers were noted on some alloys. Three temperatures were considered 880^0C, 930^0C and 980^0C with the objective of obtaining Arrhenius plots and activation energies. Evaluations were kept constant for both environments and made after 4, 49, 100 and 225 h oxidation time. Weight gain data were obtained and scale thickness measurements were made (using an image analysis system) on selected samples to constitute the kinetic data. The validity and relevance of the kinetic data obtained using these two parameters were evaluated.

Metallographic observations, SEM, EDS, EPMA, XRD, XPS, and AFM were selectively used to obtain information about the morphology and composition of the scales formed. This information was used to draw out empirical differences as a result of variations in the pO_2 and temperature.

The results indicated that the chromium content of the binary alloys determined the oxidation kinetics and oxide morphology developed (including internal oxidation) in air and low pO_2. In air, the scale compositions were further affected by the bulk chromium content. Values for the parabolic rate constant based on weight gain, k_p, for the oxidation of the binary alloys in low pO_2 ranged from 10^{-13} to 10^{-9} $g^2.cm^{-4}.s^{-1}$. The rate constant based on scale thickness, k_s, where measured, was of the order of 10^{-13} cm^2/s. The value for k_p in hydrogen/water increased with increase in temperature but the change did not appear to be as great as that observed for air oxidation. The k_p of pure chromium was higher in air than in low pO_2.

Values of k_p for the commercial alloys were within the limits quoted for chromia formers, i.e. 10^{-13} to 10^{-12} $g^2.cm^{-4}.s^{-1}$. The k_s values ranged from 10^{-14} to 10^{-13} cm^2/s. Oxidation in hydrogen/water yielded k_p values which were comparable in magnitude to air oxidation, but k_s values were lower than their air counterparts. The activation energy, Q, for the oxidation of the commercial alloys in air and low pO_2 ranged from 307 to 193.6 kJ/mol calculated using k_p. The limits of Q based on measurements of scale thickness were 266.2 and 31.1 kJ/mol.

The implications of these and other results were discussed in terms of alloy composition, exposure time and temperature, and the type of gaseous environment. Links were made to factors such as chromium content, alloy microstructure, and effect of minor additional elements on the oxidation kinetics and morphology where possible. The oxidation of the binary alloys in the hydrogen/water environment was compared to the oxidation of an alloy containing a noble metal. The effect of alloying chromium was highlighted. Variations in the kinetics were used to support different defect models for the oxidation of chromia in air and low pO_2.

The initial stages of oxidation were studied for Ni20Cr, Ni30Cr, Ni80Cr binary alloys and for one commercial alloy. This information when correlated with the effects of heating procedure on the nucleation of oxides helps elucidate the mechanism of oxide growth. The surface application of cerium and the use of Au markers and immersion in an alumina pack were additional experiments to further elucidate the mechanics of oxidation. Finally a model has been presented for the oxidation mechanism of the commercial alloys incorporating existing hypothesis regarding oxide development.

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Thesis Abstract: Thermodynamic and Dielectric Properties in Modulated Two-dimensional Electronic Systems

SEÁN STEWART

Abstract of a Thesis Submitted for the Degree of Doctor of Philosophy
at the University of Wollongong, Wollongong

In this thesis we investigate the influence of an additional periodic modulation potential which is weak, either electric or magnetic in nature, and spatially modulated along one dimension, on the equilibrium thermodynamic and dielectric response properties of a two-dimensional electron gas in the presence of an externally applied perpendicular magnetic field.

The application of an additional modulation potential results in a broadening of the Landau level energy spectrum into bands whose widths oscillate as a function of the externally applied magnetic field. Such oscillations are found to reflect the commensurability between the two different length scales present in the sys-tem, namely the cyclotron diameter at the chemical potential and the period of the modulation. We show that such commensurability effects are also to be found in all thermodynamic quantities of the system which, in the case of a magnetic modulation, are shown for the first time. They appear at low magnetic fields as an amplitude modulation of the well-known de Haas-van Alphen-type oscillations, familiar from the homogeneous two-dimensional electron gas system in an external magnetic field which may or may not be resolved depending on temperature, and are only weakly dependent on temperature. Their origin is attributed to the oscillations occurring in the bandwidths and are consequently completely different in origin from the usual de Haas-van Alphen-type oscillations. We also find that the resulting commensurability oscillations in each thermodynamic function exhibit well-defined phase relations between the electric and magnetic modulations except in the case of the orbital magnetisation and the orbital magnetic susceptibility.

The dynamical dielectric response function and collective excitations for such weak spatially modulated systems are also calculated for within the random-phase approximation. It is found that the dynamical dielectric response function is not only broadened by the additional spatial modulation, it also contains a series of subsingularities at the band edges. The origin of the new subsingularities is related to the transition energies near the van Hove singularities of the energy bands attributed to the modulation-induced broadening of the energy spectrum. This broadening, being non-uniform, leads to the reintroduction of particle-hole pair excitations into the dielectric response function. Such broadening of the response function is also found to modify the magnetoplasmon modes of such systems over their unmodulated counterpart. The broadened Landau levels allow for a new low-frequency intra-magnetoplasmon mode to occur which exhibits oscillatory behaviour as a function o-l the external magnetic field. It is also shown that additional modulation-

induced oscillations occur in the inter-magnetoplasmon spectrum, which is split into the principal and the Bernstein modes. All such oscillations reflect the ubiquitous commensurability oscillations now found in these weakly modulated systems as a function of the external magnetic field.

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Thesis Abstract: "Where The Spirits Meet" A History of The National Museum And Art Gallery, Waigani, Papua New Guinea

CHRISTINA WRIGHT

Abstract of a Thesis submitted for the Degree of Master of Arts (Hons)
at the Charles Sturt University, Bathurst Campus

This thesis examines the history of collecting cultural material during the first century of colonial impact, 1884-1984, beginning with the British colonization of the territory in 1884; the use of temporary museums established in Papua by Australian government officials after it was proclaimed a Territory of the Commonwealth in 1906; to the Independent State of Papua New Guinea in 1975 followed by the establishment of the permanent Papua New Guinea National Museum at Waigani in 1977.

The notion of a museum was brought to Papua and New Guinea with the English language by government officials, explorers and missionaries who came for a variety of reasons. The new residents of the islands began collecting specimens of cultural material regarded as 'curios' from the colony before it was greatly altered or completely lost with the encroachment of European civilization. Many of these artefacts are stored in museums and private collections throughout the world. A small band of the government officials collected cultural material with the intention that it be returned at a later time to Papua New Guinea.

In traditional times village societies had special places for particular and religious artefacts associated with their way of life. The goal of the carvers and artists was not noble simplicity but multiplicity of visions, as the objects combined formal discipline with diversity of motifs for their own needs. Nothing was left to chance: to the villagers, all things were linked and merged into one another. The term 'museum', a building used for the storage and exhibition of objects, has been embraced by Papua New Guineans to take over the functions of their own traditional communal houses. This pre-existing cultural attitude towards collections of objects of social importance made the western 'museum culture' easy for Papua New Guineans to assimilate.

Early colonial officers, such as MacGregor, Murray, Cleland, McCarthy and others established policies that sought to protect and preserve the country's cultural heritage until Papua New Guineans could implement their own cultural policies for the nation. These early 'Heads of Government' took advantage of the work done by the anthropologists, Haddon, Pitt-Rivers, Seligman, Williams and others in seeking to understand the ways of the indigenous people of the new colony. The role played by the professionals (both from outside the Museum and as employees) has been very influential in enlisting Australian and international aid, including UNESCO support. Despite the good intentions behind the National Cultural Property (Preservation) Act to protect the country's cultural heritage, the Museum has encountered many difficulties in enforcing the law.

When contrasting the position between Papua New Guinea's National Museum and museums of other Pacific nations, it can be seen that early colonial officials in Papua New Guinea have been most supportive and protective of the culture and the development of museums for the people. This has not always been the case with other Pacific Islands. There were times when those involved with the National Museum succeeded in their objectives and other times when some poor decisions were made. However, the basic policies of promoting national identity and encouraging people's pride in their own individual cultures has always been of paramount importance to those involved with the Museum. The Constitution of the Nation acknowledges the noble traditions passed from one generation to another. (See Appendix 1)

After Independence, the historical account of the progressive development of the Papua New Guinea National Museum was followed by a setback in 1984 when the Head of Government support was withdrawn and funding to the Museum severely cut.

It will be seen that the Papua New Guinea National Museum has been forged out of British Imperial culture and early colonial foresight. There has been a blending of 'native' and European cultures by Papua New Guineans to meet their own particular cultural needs. Sir Bernard Narokobi, while President of the Museum Board of Trustees, said 'We should start with our ways and make use of other people's ways to uplift and improve upon our ways'[1]

The Museum reflects the nation's cultural background aesthetically and spiritually and it '... stands as a monument to the past, a source of study to the present and an inspiration to the future.[2] It is a place '**where the spirits meet**'.[3]

Notes

1. C. B. Narokobi, The Melanesian Way: Total Cosmic Vision of Life, Institute of PNG Studies, Port Moresby, 1980, p.12.
2. Michael Somare, President, board of Trustees, Papua New Guinea Public Museum and Art Gallery, Annual Report of the Trustees, 1975-76,

   Port Moresby, p.ii.
3. Mr Geoffrey Mosuwadoga, in discussions with Mrs. Chris Wright, referred to the National Museum as the place '**where the spirits meet**'.

Appendix 1

The following extract from: **"The Constitution of the Independent State of Papua New Guinea"** acknowledges the noble traditional wisdoms passed from one generation to another:

"We the people of Papua New Guinea

> United in one nation
>
> Pay homage to the memory of our ancestors — the source of our strength and origin of our combined heritage
>
> Acknowledge the worthy customs and traditional wisdoms of our people — which have come down to us from generation to generation
>
> Pledge ourselves to guard and pass on to those who come after us, our noble traditions..."

Therefore let us live and be guided by our Constitution.

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Annual Report of Council

For the Year Ended 31st March 1999

PATRONS

The Council expresses its gratitude to His Excellency the Honourable Sir William Deane AC, KBE, Governor General of the Commonwealth of Australia, and to His Excellency the Honourable Gordon Samuels AC, Governor of New South Wales, for their continuing support as Patrons of the Society.

MEMBERSHIP

The membership of the Society at 31st March 1999 comprised: Patrons 2, Honorary Members 14, Members 259, Associates and Spouse Members 21.

Eight members resigned from and 33 new members were admitted to the Society during the year.

The deaths of the following longstanding members were announced with regret: Dr F.D. McCarthy (1949*; Hon. Member 1979), Prof. S.C. Haydon (1965)*, and Mr J.N.G. Grant (1961)*.

* (Year) of admission to the Society.

OFFICE

The Society continued during the year to lease for its office and library a half-share of Convocation House, 143 Herring Road, North Ryde, on the campus of Macquarie University. Council is grateful to the University for continuing the lease. Council greatly appreciates the ongoing secretarial assistance provided by Mrs V. Chandler.

MEETINGS

Nine General Monthly Meetings, five Special Meetings and Events and the 131st Annual General Meeting were held in Sydney during the year. The Southern Highlands Branch held eleven meetings; the New England Branch none. Summaries of these meetings are presented in ABSTRACTS OF PROCEEDINGS, below.

Eleven Meetings of Council were held at the Society's offices at North Ryde.

PUBLICATIONS

Journal

Volume 131 Parts 1, 2, 3 and 4 of the *Journal and Proceedings of the Royal Society of New South Wales* were published for the year 1998.

The volume contained the 31st Liversidge Research Lecture 1998, the Presidential Address, six peer-refereed research papers on geology (stratigraphy/structures), mineralogy (incl. a meteorite), history (biographical), ten abstracts of Higher Degree theses covering a wide variety of subjects (including zoology, mathematics, DNA, agriculture, physics, medicine, biochemistry and human geography). The Council Report for 1997/98, the Financial Statement for 1997, biographical memoirs and citations for Awards for 1997 were also included.

Council wishes to thank all the voluntary referees who assessed papers offered for publication. The Society received applications seeking permission to reproduce material from its *Journal and Proceedings*.

Bulletin

Ten issues of the *Bulletin* were produced during the year. The Council wishes to thank the many authors who contributed material. Particular thanks are extended to Ted O'Keeffe for production of the *Bulletin* and to the individuals who assist in mailing the issues.

LIBRARY

As in previous years, acquisitions of literature, usually journals, but occasionally books, and reports, etc. in series, has been maintained throughout 1998. The exchange and gifts agreements are arranged and monitored at the Society's office at North Ryde by the Honorary Librarian. Exchange material from overseas and some Australian literature are sent directly by the originator to the Dixson Library at the University of New England, Armidale NSW. Remaining Australian material is added to the collection at Herring Road. A few exchange agreements have been cancelled, due in some instances to economic problems or lack of shelf space at the recipient organisations.

Publications received at the Dixson Library on behalf of the Society are processed and integrated into the general collection, but are marked with the Royal Society of New South Wales insignia on the spine of each bound volume.

Council thanks Mr Karl Schmude, University Librarian, University of New England and his staff — particularly Mrs Helen Stokes — for their continued efficient care of the Society's collection in the Dixson Library.

Some very well-produced reports, journal issues and beautiful maps (mainly geological) have been received recently in the library at Herring Road. Displays of literature has been mounted in the office library. Accession Lists of this material are being published in the *Bulletin*. Members are welcome to visit the office by appointment and to inspect recent acquisitions. Thanks are due to Mrs Victoria Chandler for her care and assistance in the library work.

AWARDS

The following awards were made for 1998 and presented at the Annual Dinner in March1999:

Royal Society of New South Wales Medal

(For achievements in science and service to the Society) - Dr. David F. Branagan, School of Geosciences, University of Sydney.

Clarke Medal (in Geology)

Emer. Prof. Richard L. Stanton AO, Dept. of Geology, University of New England, Armidale NSW.

Walter Burfitt Prize

(For scientific work done in Australia or New Zealand) - Prof. Anthony K. Burrell, School of Chemistry, Massey University, Palmerston North, New Zealand.

The James Cook Medal, the Edgeworth David Medal and the Archibald D. Ollé Prize were not awarded for 1998.

SUMMER SCHOOL

A two day Summer School, attended by 39 Year 11 students from both private and public schools, was organised in January 1999 at Royal Prince Alfred Hospital (one day) and the Australian Nuclear Science and Technology Organisation, Lucas Heights (the second day). The theme, "Application of Radioactivity in Medicine and Industry" was suggested by Dr. G.C. Lowenthal AM, who also organised the program. Members of both RPAH and ANSTO gave time and effort to lectures, displays and instruction, for which Council of the Society expresses its sincere thanks.

NEW ENGLAND BRANCH

The representative for the Branch reported the intention of the Branch to create a focal point for local Armidale citizens' interest in science in connection with a reconstruction and revitalisation of the Branch.

SOUTHERN HIGHLAND BRANCH

The branch expanded its activities during 1998, moving the venue for meetings to the Frensham School lecture theatre, (seating capacity of 110-130), thanks to the understanding of the Board of Winifred West Schools Ltd.

Six new members joined the branch during the year. The Branch's 1998 Science Award winner was Miss Sarah Cush, of Chevalier College, Bowral.

At the Branch's Annual General Meeting, (12th March 1998) the following were elected to the Branch's Committee for 1998/99:-

Chairman:	David J. Robertson CBE
Vice-Chairmen:	Dr K.G. McCracken AO Mr Roy Perry
Hon. Treasurer:	Miss C.M. Staubner
Hon. Secretary:	Mr C.F. Wilmot

ABSTRACTS OF PROCEEDINGS

SPECIAL MEETINGS AND EVENTS

1st April 1998

The 1071st General Monthly Meeting and the 131st Annual General Meeting were held at the Australian Museum, Sydney. The President Dr E.C. Potter was in the Chair and 30 members and visitors attended. The Annual Report of Council and the Financial Report for 1997-1998 were adopted. Mr B.E. Holden was elected auditor for 1998-1999.

The following Awards for 1997 were announced:

Royal Society of New South Wales Medal
  Mr Edward Donald O'Keeffe, School of Mathematics, Macquarie University, Hon. Editor of the Society's *Bulletin*.
Clarke Medal (in Botany)
  Dr Charles Barry Osmond, Research School of Biological Sciences, Australian National University.
Edgeworth David Medal
  Assoc./Prof. Albert Y.H. Zomaya Dept. of Electronic Engineering, University of Western Australia.
Archibald Ollé Prize
  Dr Gerrit Neef, Dept. of Applied Geology, University of New South Wales.

The following members were elected to the 1998-1999 Council:

President	Dr D.J. O'Connor
Vice-Presidents	Dr E.C. Potter Dr D.F. Branagan Dr G.C. Lowenthal Prof. W.E. Smith Prof. D.J. Swaine
Hon. Secretaries	
General	Dr M.R. Lake
Editorial	Mrs M. Krysko v. Tryst
Hon. Treasurer	Dr P.R. Evans
Hon. Librarian	Miss P.M. Callaghan
Members of Council	
	Assoc. Prof. A.T. Baker

Members of Council (cont.)
Mr J.R. Hardie
Dr F.L. Sutherland
Emer. Prof. R. Vernon
Prof. M. Wilson
New England Representative
Mr B.B. Burns
Southern Highlands Representative
Dr K.G. McCracken.

Dr Potter yielded the chair to the incoming President, Dr D.J. O'Connor, who thanked the outgoing Council members for their contributions during the preceding year. Dr Potter then presented his annual Presidential Address, "Applied Scientific Research – I Did It My Way".

30th April 1998
A half day seminar offering seven talks on "French Cooperation in Engineering at the UNSW", sponsored by the Australian-French Association for Professional and Technical Specialists and the Royal Society of New South Wales.

2nd June 1998
Members attended the 200th Anniversary Service commemorating Rev. W.B. Clarke's birthday at the St. Andrew's Cathedral, Sydney. The President, Dr D.J. O'Connor contributed a speech to the service.

1st July 1998
The 31st Liversidge Research lecture in chemistry entitled "New Molecular Receptors for Small Molecules and Ions" was delivered by Professor L.F. Lindoy of the School of Chemistry, University of Sydney at the 1074th General Monthly Meeting. About 30 members and visitors attended.

26 November 1998
Under the auspices of the Royal Society of New South Wales, the Australian Museum Geodiversity Research Centre and the Copy Right Publishing Co. the book by John C. Grover OBE, a member of the Society, entitled "Volcanic Eruptions and Great Earthquakes" was launched by Dr F.L. Sutherland, also a member of the Society.

9th February 1999
A joint meeting of four societies: Australian Institute of Energy, Australian Nuclear Association, The Institute of Engineers Australia and The Royal Society of New South Wales met at Eagle House Sydney. Prof. Michael Wilson, Head of the Department of Chemistry, Materials and Forensic Science, University of Technology, Sydney delivered an address on "Materials for an Energy-effective Future" that dealt with the fourth form of the element carbon — the only new one discovered since ancient times — fullerenes and nanotubes.

16th March 1999
The Annual Dinner of the Society was held at the Royal Sydney Yacht Squadron, Kirribilli. The guest speaker was Prof. Lesley Johnson, Pro-Vice Chancellor (Research) of the University of Technology, Sydney. 45 members and friends attended.

GENERAL MONTHLY MEETINGS

1st April 1998
The 1071st General Monthly Meeting was held at the Australian Museum, Sydney immediately prior to the 131st Annual General Meeting (see SPECIAL MEETINGS AND EVENTS, above).

6th May 1998
The 1072nd General Monthly Meeting was held at the Australian Museum, Sydney and addressed by Clinical Assoc. Prof. M.J.

Fulham, Director of the Department of Positron Emission Tomography (PET) and Nuclear Medicine, Royal Prince Alfred Hospital, Camperdown, Sydney, on "Functional Imaging in the Neurosciences".

Dr. G.C. Lowenthal proposed a vote of thanks.

3rd June 1998

The 1073rd General Monthly Meeting, held at the Society's Office in Herring Rd, North Ryde to discuss three changes to the Society's Constitution as proposed by Council. The number of members attending (18) was insufficient to constitute a quorum, so no formal votes were taken, but informal polls indicated that two thirds of those present were in favour of all three proposals. Council is considering what further steps should be taken.

1st July 1998

The 1074th General Monthly Meeting was held at the School of Chemistry, University of Sydney, where Prof. L.F. Lindoy delivered the 31st Liversidge Research Lecture (see SPECIAL MEETINGS AND EVENTS, above).

5th August 1998

The 1075th General Monthly Meeting was held in the Edgeworth David Building, University of Sydney, as a Joint Meeting with the Linnean Society of NSW and the NSW Branch of the Geological Society of Australia to commemorate the Bicentenary of Rev. W.B. Clarke's birth. Three speakers addressed the Meeting: Prof. K.J. Cable on "Clarke the Cleric", Mr Michael Organ on "The Rev. W.B. Clarke (1798–1878) – what did he actually do?", and Dr David Branagan on "Not forgetting Stutchbury (1798–1859) and Keene (1798–1872)".

8th September, 1998

The 1076th General Monthly Meeting was held at the School of Physics, University of Sydney, as a Joint Meeting with the Australian Institute of Physics. Dr B.A. Pailthorpe, Dept. of Applied Physics, Sydney Vislab, University of Sydney and San Diego Super Computer Center USA, addressed members and visitors on "Applications of High Performance Computing and Communication".

7th October 1998

The 1077th General Monthly Meeting was held at the University of Technology, Sydney. Assoc. Prof. A.T. Baker, Dept. of Chemistry, Materials and Forensic Science, University of Technology Sydney, delivered an address entitled "Dwyer and Lions Revisited: Complexes of Sexadenta Ligands". Dr E.C. Potter offered a vote of thanks.

4th November 1998

The 1078th General Monthly Meeting was held at the Australian Museum. It took the form of a Joint Meeting with ANZAAS. the general topic, "Recent Research in Limestone Caves", was covered by three speakers: Dr Craig Barnes, "Physical Processes in Caves", Mr Neville Michie, "Radon in Caves" and Ms Jill Rowling, "Ribbon Helictites".

SOUTHERN HIGHLANDS BRANCH

12th March 1998

Following the Annual General Meeting, Prof. S. Touyz addressed 37 members and visitors on Anorexia Nervosa, the third most common illness in teenage girls.

23rd April 1998

Emer. Prof. D..J. Mulvaney AO, CMG presented to 49 members an address entitled

"The Overland Telegraph and the Dawn of Australian Anthropology".

21st May 1998
Mr J. Swainston of Maxwell Optical Industries and formerly of Bell & Howell (Aust.) spoke to an attendance of 39 members and visitors on the history of imaging - "From *Camera Obscura* to Digital".

28th May 1998
[Special Event] A joint meeting with the National Parks Association, The Wildlife Information and Rescue Service and the Robertson Environmental Protection Society. Dr J. Wamsley spoke on the general failure to save endangered species and his efforts to reverse the trend in his successful sanctuaries covering 70 000 hectares, from which feral animals and exotic plant species are excluded. The lecture, held at Oxley College's Hoskins Hall, was attended by 105 members and visitors.

25th June 1998
Assoc. Prof. D. Celemajer, Cardiologist of Sydney University, Royal Prince Alfred Hospital and the Childrens Hospital, Westmead, spoke to an audience of 70 members and visitors on his recent discoveries about the causes of atherosclerosis.

23rd July 1998
Dr D. Russell, Department of General Philosophy, Sydney University, spoke on "Visions of Madness" to an interested audience of 69 members and visitors. She pointed out that markedly different perceptions of madness have been maintained in western culture and that contemporary views in terms of faulty biology may also be short-lived.

20th August 1998
Dr M. Gore, Director of Questacon, Canberra, spoke to 130 members and visitors, including 40 students from Frensham School, on "Unexpected Science" – presented in the form of a rapid succession of brain-teasing demonstrations of surprising simplicity, but with significant implications.

24th September 1998
Dr R. Binns, CSIRO Exploration and Mining, presented a lecture on "Mineral Deposits on the Ocean Floor: Mines in the Making" to 60 members and visitors.

22nd October 1998
Dr D. Mills, physicist of Sydney University and former President of the International Solar Energy Society, spoke to 85 members and visitors on, "Solar Thermal Energy; the Environmental Cinderella". The Society's President Dr D.J. O'Connor and immediate past-President Dr E. Potter also attended, prior to holding the following day a fruitful, informal meeting with the Branch Committee on a number of issues.

19th November 1998
Dr A. Parker, from the Division of Invertebrate Zoology, Australian Museum, presented an address on, "Structural Colour in Animals, Living and Extinct", relating the appearance of diffraction gratings in some marine animals to the 'Cambrian Explosion' in evolution. 53 members and visitors were present. Prior to the meeting, Branch Vice President Mr R. Perry spoke about the Branch's 1998 Science Award for High School Students and invited Dr Parker to present the Award to the winner, Miss Sarah Cush of Chevalier College.

18th February 1999
Dr G. Pearman, of CSIRO Atmospheric Research, addressed 127 members and visitors on further developments in global warming. Australia's position regarding the Kyoto Protocol was discussed.

FINANCIAL REPORT FOR THE YEAR ENDED 31 DEC 1998

Your Council members submit the following financial statements of the Society for the year ended 31 Dec 1998.

COUNCIL MEMBERS

The names of Council members throughout the year and as at the date of this report are:

A/Prof. A.T. Baker
Dr D.F. Branagan
Miss P.M. Callaghan
Dr P.R. Evans
Mr J. Hardie
Mrs M. Krysko v. Tryst
Dr M. Lake
Dr G.C. Lowenthal
Dr D.J. O'Connor
Dr E.C. Potter
Prof. W.E. Smith
Dr F.L. Sutherland
Prof. D.J. Swaine
E/Prof. R.H. Vernon
Prof. M.A. Wilson

PRINCIPAL ACTIVITIES

The principal activities of the Society during the year were: organisation of meetings; publication of the *Journal and Proceedings* and the *Bulletin*; organisation of a Summer School.

SIGNIFICANT CHANGES

No significant change in the nature of these activities occurred during the year.

OPERATING RESULT

The loss for the year amounted to $1998.

Signed in accordance with a resolution of the Members of the Committee.

President .... (Original signed D.J. O'Connor)

Hon. Treasurer ....(Original signed P.R. Evans)

Dated this 31st day of March 1999

INCOME & EXPENSE AT 31 DECEMBER 1998

	1998 $	**1997** $
INCOME		
Membership Subscriptions	12278	14319
Applications for Membership	164	158
	12442	14477
Less Provision for Doubtful Debts	1803	1910
Total Membership Income	10639	12567
Journal Subscriptions	8083	7446
Total Membership and Journal Income	18722	20013
Reprints & Other Publications	245	239
Investment Income	5787	6691
Research Fees	0	10
Summer School	2722	0
Annual Dinner	177	148
	27653	**27101**
EXPENSES		
Accountancy and Audit Fees	4765	4400
Bank Charges and Government Duties	111	68
Bulletin Publication and Distribution	2071	2531
Depreciation	436	529
Entertainment Expenses	0	282
Insurance	787	784
Journal & Proceedings Publication and Distribution	10228	10271
Miscellaneous	64	46
Monthly Meetings	389	292
Postage	502	625
Printing and Stationery	340	621
Rent	2000	2000
Repairs	0	8
Salaries	7319	7642
Superannuation Contributions	201	448
Telephone	439	492
	29651	**30859**
LOSS FOR THE YEAR	**1998**	**3758**
Balance at 1 January	114529	118287
Balance at 31 December	112531	114529

FINANCIAL REPORT FOR THE YEAR ENDED 31 DEC 1998 (cont.)

BALANCE SHEET AT 31 DECEMBER 1998

	NOTES	1998 $	1997 $
ASSETS			
CURRENT ASSETS			
Cash	2	13958	10607
Receivables	3	1962	4810
Investments	4	183	183
TOTAL CURRENT ASSETS		16103	15518
NON-CURRENT ASSETS			
Investments	4	132509	135500
Property, Plant & Equipment	5	15565	15962
TOTAL NON-CURRENT ASSETS		148074	151462
TOTAL ASSETS		164177	**166980**
LIABILITIES			
CURRENT LIABILITIES			
Creditors and Accruals	6	5647	7623
Other	7	2728	2971
TOTAL CURRENT LIABILITIES		8375	10594
NON-CURRENT LIABILITIES			
Creditors and Accruals	7	23	39
TOTAL NON-CURRENT LIABILITIES		23	39
TOTAL LIABILITIES		**8398**	**10633**
NET ASSETS		**155779**	**156429**
MEMBERS' FUNDS			
Library Reserve	8	7311	7311
Library Fund	9	12976	12325
Trust Funds	10	22961	22264
Accumulated Funds		112531	114529
TOTAL MEMBERS' FUNDS		**155779**	**156429**

The accompanying notes form part of these financial statements.

NOTES TO AND FORMING PART OF THE ACCOUNTS FOR YEAR ENDED 31 DECEMBER 1998

1 STATEMENT OF ACCOUNTING POLICIES

These financial statements are a special purpose financial report prepared for use by the council and members of the Society. The council has determined that the Society is not a reporting entity.

The statement has been prepared in accordance with customary accounting practices. The statements are also prepared on an accruals basis. They are based on historic costs and do not take into account changing money values or, except where specifically stated, current valuations of non-current assets.

The following specific accounting policies, which are consistent with the previous period unless otherwise stated, have been adopted in the preparation of these statements:

a) Non-Current Investments

Investments are brought to account at cost. The carrying amount of investments is reviewed annually to ensure it is not in excess of the recoverable amount of the investments.

b) Property, Plant & Equipment

Plant and equipment is brought to account at cost or at independent valuation, less, were applicable, an accumulated depreciation or amortisation.

The depreciable amount of all fixed assets is depreciated over their useful lives commencing from the time the asset is held ready for use.

The exception to the above policy is the society's library, which is brought to account at its 1936 independent valuation, a more recent valuation not being available.

c) Where required, comparative figures have been adjusted to conform with changes in presentation for the current financial year.

		1998 **$**	**1997** **$**
2	**CASH**		
	Cash on hand	68	62
	Cash at bank	13890	10463
		13958	10525
3	**RECEIVABLES**		
	Membership Subscriptions in arrears	2653	3501
	Less provision for doubtful debts	2653	3501
		0	0
	Debtors for contributions towards printing *Journal* and Proceedings	1981	1938
	Other debtors	0	2872
		1981	4810

FINANCIAL REPORT FOR THE YEAR ENDED 31 DEC 1998

NOTES TO AND FORMING PART OF THE ACCOUNTS FOR YEAR ENDED 31 DECEMBER 1998 (cont.)

		1998 $	1997 $
4	**INVESTMENTS**		
	Current		
	Deposits at call	183	183
	Non-Current		
	Interest-bearing deposits	132509	135500
5	**PROPERTY, PLANT & EQUIPMENT**		
	Office equipment and furniture -at valuation of	10000	10000
	less accumulated depreciation	8045	7648
		1955	1542
	Library - at 1936 valuation	13600	13600
	Pictures - at cost less accumulated depreciation	10	10
		15565	15962
6	**CREDITORS & ACCRUALS**		
	Sundry creditors and accruals	5647	7623
7	**OTHER LIABILITIES**		
	Current		
	Life Members subscriptions prepaid	16	16
	Membership subscriptions paid in advance	98	75
	Journal & Proceedings subscriptions paid in advance	2578	2880
		2692	2971
	Non-Current		
	Life Members subscriptions prepaid	23	39

		NOTES	1998 $	1997 $
8	**LIBRARY RESERVE**			
	Balance at 1 January		7311	7311
	Movement for year		0	0
	Balance at 31 December		7311	7311
9	**LIBRARY FUND**			
	Balance at 1 January		12325	10739
	Donations and interest		671	1586
			12996	12325
	Library purchases and expenses		20	0
	Balance at 31 December		12976	12325
10	**TRUST FUNDS**			
	Included in the Trust Funds are			
	Clarke Memorial Fund	11	3190	3027
	Walter Burfitt Prize	12	7605	7202
	Liversidge Bequest Fund	13	3583	3434
	Ollé Bequest Fund	14	8583	8601
	Total Trust Funds		22961	22264
11	**CLARKE MEMORIAL FUND**			
	Capital		5000	5000
	Revenue			
	Income		170	184
	Expenditure		(7)	(175)
	Surplus		163	9
	Balance at 1 January		(1973)	(1982)
	Balance at 31 December		(1810)	(1973)
	Total Capital and Revenue		3190	3027

FINANCIAL REPORT FOR THE YEAR ENDED 31 DEC 1998

NOTES TO AND FORMING PART OF THE ACCOUNTS FOR YEAR ENDED 31 DECEMBER 1998 (cont.)

	1998 $	1997 $
12 WALTER BURFITT PRIZE FUND		
Capital	3000	3000
Revenue		
Income	403	414
Expenditure	0	0
Surplus	403	403
Balance at 1 January	4202	3788
Balance at 31 December	4605	4202
Total Capital and Revenue	7605	7202
13 LIVERSIDGE BEQUEST FUND		
Capital	3000	3000
Revenue		
Income	192	197
Expenditure	43	0
Surplus	149	197
Balance at 1 January	434	237
Balance at 31 December	583	434
Total Capital and Revenue	3583	3434
14 OLLÉ BEQUEST FUND		
Capital	4000	4000
Revenue		
Income	482	494
Expenditure	500	0
Surplus (Deficit)	(18)	494
Balance at 1 January	4601	4107
Balance at 31 December	4583	4601
Total Fund Capital and Revenue	8583	8601

STATEMENT BY MEMBERS OF THE COUNCIL

In the opinion of the committee the financial statements:

1 present fairly the financial position of The Royal Society of New South Wales as at 31 December 1998 and the results for the year ended on that date in accordance with Australian Accounting Standards and other mandatory professional reporting requirements;

2 at the date of this statement, there are reasonable grounds to believe that the Society will be able to pay its debts as and when they fall due.

This statement is made in accordance with a resolution of the Council and is signed for and behalf of the Council by:

President ....(Original signed D.J. O'Connor)

Hon. Treasurer ....(Original signed P.R. Evans)

Dated this 31st Day of March 1999

FINANCIAL REPORT FOR THE YEAR ENDED 31 DEC 1998

INDEPENDENT AUDIT REPORT TO MEMBERS

Scope

I have audited the financial statements being the Statement of Income and Expenditure, Balance Sheet, and Notes to and forming part of the financial statements of The Royal Society of New South Wales for the year ended 31 December 1998. The Council is responsible for the financial statements. I have conducted an independent audit of these financial statements in order to express an opinion on them to members.

My audit has been conducted in accordance with Australian Auditing Standards to provide reasonable assurance as to whether the financial statements are free of material misstatement. My procedures included examination on a test basis, of evidence supporting the amounts and other disclosures in the financial statements, and the valuation of accounting policies and significant accounting estimates. These procedures have been undertaken to form an opinion as to whether, in all material respects, the financial statements are presented fairly in accordance with Australian Accounting Standards and other mandatory professional reporting requirements so as to present a view which is consistent with my understanding of the Society position and the results of its operations.

The audit opinion expressed in this report has been formed on the above basis.

Audit Opinion

In my opinion, the financial statements present fairly in accordance with Australian Accounting Standards and other mandatory reporting requirements the financial position of The Royal Society of New South Wales as at 31 December 1998 and the results of its operations for the year then ended.

B.E. HOLDEN FCA (Original signed B.E. Holden
Chartered Accountant 31st March 1999)
Chatswood

Participants in the Summer School on
"Application of Radioactivity in Medicine and Industry", 18 – 19th January 1999

CITATIONS FOR AWARDS

THE SOCIETY'S MEDAL FOR 1998

David Francis Branagan

The Society's Medal is given for the advancement of science and contributions to the Society.

David Francis Branagan graduated from the University of Sydney with a BSc in 1951. After a varied career, including teaching and opera singing overseas, he returned to the Department of Geology and Geophysics at Sydney University in 1958 to take up the Coal Research Fellowship, which he held until 1960, and to complete an MSc on the geology of the Western Coalfield of the Sydney Basin.

In 1960 he was appointed Lecturer and completed his PhD in 1963 on a coal-related topic. He was appointed Senior Lecturer in 1965 and Associate Professor in 1975. David's scientific interests are wide and cover an extensive range, including the geology of the Sydney Basin, engineering geology, geomorphology, remote sensing, rock art, the history of geology and environmental geology, all of which he has continued to pursue since his retirement in 1989.

During almost 30 years as an academic, David made pioneering contributions to the development of Engineering Geology. He influenced a whole generation of civil engineers and introduced geology students to different ways of applying their science. His work on numerous government committees helped establish the significance and relevance of the field.

David was also a pioneer in environmental geology. He was probably the first geologist in Australia to give evidence for an environmental cause in a court case.

David's interest in the history of geology produced two histories of the Department of Geology and Geophysics and ongoing work on notable Australian geologists, including David, Clarke, Selwin, Stutchbury and Tenison Woods.

David promoted geology in schools and to the general public by writing a text book, serving on examination committees and producing, with Gordon Packham, two editions of a field guide to New South Wales geology.

David has been a member of the Society since 1963. He has served on the Society's Council, as President and Vice President. He made a particular contribution by introducing new technology to the preparation of the *Journal and Proceedings*. David continues to actively participate in music, sport (particularly athletics and swimming) and the church.

David Branagan's many achievements in a wide range of fields show him to have not only advanced Science and served the Society, but also to have more completely than most fulfilled the Society's aim of encouraging "studies and investigations in Science, Arts, Literature and Philosophy", which, since its inception, has been the purpose of the Society.

David Francis Branagan is a most worthy recipient of the Society's Medal.

P.R.E.

THE CLARKE MEDAL FOR 1998

Richard Limon Stanton

Richard Limon Stanton AO, MSc PhD FAA, Emeritus Professor of Geology at The University of New England, is one of Australia's most distinguished geologists. In addition to the Clarke Medal, Professor Stanton has received three other major awards of the Royal Society of New South Wales, namely the Clarke Memorial Lectureship (1985), The Ollé Prize (1956) and the Society's Medal (1973). His numerous other distinctions include the Haddon Forrester King Medal of the Australian Academy of Science (1999), the Penrose Medal of the Society of Economic Geologists (1993), the Browne Medal of the Geological Society of Australia (1990), the William Smith Medal of the Geological Society of London (1987), the Goldfields Gold Medal of the Institution of Mining and Metallurgy, London (1976), the President's Award of the Australasian Institute of Mining and Metallurgy (1974) and the David Syme Research Prize of The University of Melbourne (1972). He is an Honorary Fellow of the Institution of Mining and Metallurgy, the Geological Society of America and an Honorary Member of the Royal Society of New South Wales.

Professor Stanton has published many papers on ore deposits and related rocks, and is especially well known for his work on sulphide microstructures and his book "Ore Petrology" (1972), which was a landmark publication, placing ore bodies into an appropriate petrological context. He has continued this approach with his more recent book "Ore Elements in Arc Lavas" (1994). He plans to continue his research into volcanogenic ore deposits and their host rocks at the Australian National University, working with our Clarke Lecturer for 1999, Professor Richard Arculus.

Professor Stanton is a very worthy recipient of the Clarke Medal of the Royal Society of New South Wales.

R.H.V.

THE WALTER BURFITT PRIZE FOR 1998

Anthony K. Burrell

The Walter Burfitt Prize is awarded to an Australian or New Zealand scientist "whose papers and their contributions published during the past six years are deemed of the highest scientific merit."

The Prize for 1998 is awarded to Professor Anthony K. Burrell for his research in the field of chemistry. He is a staff member of Massey University, Palmerston North, New Zealand.

Photosynthesis is a very complex process, which is the subject of much ongoing research, for example, in the field of electron transfer to and from porphyrins. Burrell has studied various systems which have led to a building block strategy for the one-step construction of large porphyrin arrays from porphyrin monomers. This could be relevant to the making of photovoltaic cells using large arrays of synthetic porphyrins.

The synthesis of dimeric porphyrins linked by a ferrocene was carried out by Burrell in 1997. Such porphyrin-ferrocene conjugates are potentially important, for example, in the fields of chemical sensors and solar energy conversion. His studies are improving the understanding of how natural light harvesting arrays perform. His ultimate aim is to duplicate their properties and thereby form novel catalytic systems, new photovoltaic devices and molecular photonic assemblies.

Professor Burrell is actively engaged in another area of research, namely, the chemistry of imido complexes, for example, those of ruthenium (II) and technetium. Those complexes are relevant to methane activation and hydrocarbon amination.

Professor Burrell has an active research group and he teaches several courses in inorganic chemistry and spectroscopy. His publications are mainly in well-respected overseas journals and he is frequently invited to conferences in New Zealand, Australia and the USA. He has been most successful in the number and size of research grants which he and his co-workers have received.

It is clear that Professor Burrell is in the forefront of theoretical and practical aspects of porphyrin research, especially in relation to artificial photosynthesis. He is established as one of New Zealand's top chemists. His collaboration is sought not only for his intellectual talent, but also for his ability to finish projects in an innovative way.

The Council of the Royal Society of New South Wales is pleased to award the Walter Burfitt Prize for 1998 to Professor K. Burrell on the basis of his outstanding scientific achievements.

D.J.S.

BIOGRAPHICAL MEMOIRS

Frederick David McCarthy
1905-1997

(Photographer - Ric Bolzan. By courtesy of the Australian Museum)

Fred McCarthy's contribution to the development of Australian prehistory, in particular the study and classification of Aboriginal tool-making, is unsurpassed. During his lifetime he published more than 300 works, the best known of which, the co-authored *The Stone Implements of Australia* (1946), is still regarded as a classic. It contained the first attempt to classify Aboriginal stone tools using indigenous rather than European terminology.

He began his career at the Australian Museum in Sydney in 1920, and 12 years later, was appointed Curator of Ethnology.

In 1948 McCarthy joined the American-Australian scientific expedition to Arnhem Land led by Charles Mountford and worked closely with Margaret McArthur on *The Time Factor in the Aboriginal Quest for Food,* a paper which remains a classic reference today.

In 1958 McCarthy spent many months in north-west Australia studying Aboriginal art on a Wenner-Gren Foundation grant. A Nuffield (Australia) Foundation grant allowed him to carry out a similar study in central western NSW. In 1961 he recorded totemic clan dances at Aurukun, Cape York, Queensland.

In 1964 he was appointed Foundation Principal of what was then called the Australian Institute of Aboriginal Studies in Canberra (now known as the Australian Institute of Aboriginal and Torres Strait Islander Studies) from where he retired in 1971. McCarthy was a member of many learned societies. He served on the Council of the Royal Society of NSW for nine years, was President in 1956 and was elected an Honorary Member in 1979. On 18 April 1980 he received an Honorary Doctorate of Sciences from the Australian National University, Canberra. In 1990 he was made a Fellow of the Australian Academy of the Humanities in recognition of his services to anthropology.

His wife died in 1985. He is survived by their children, Martin, Susan and David, and grandchildren.

K.K.

NOTICE TO AUTHORS

Manuscripts should be addressed to the Honorary Secretary, Royal Society of New South Wales, PO Box 1525, Macquarie Centre, NSW 2113. Manuscripts submitted by a non-member (through a member) will be reviewed by the Hon. Editor, in consultation with the Editorial Board, to decide whether the paper will be further considered for publication in the Journal.

Manuscripts are subjected to peer review by an independent referee. In the event of initial rejection, manuscripts may be sent to two other referees.

Papers, other than those specially invited by the Editorial Board on behalf of Council, will only be considered if the content is substantially new material which has not been published previously, has not been submitted concurrently elsewhere, nor is likely to be published substantially in the same form elsewhere. Well-known work and experimental procedure should be referred to only briefly. Short notes and letters to the Editor may also be submitted for publication.

Three, single sided, typed copies of the manuscript (double spacing) should be submitted on A4 paper.

Captions to illustrations and a Table of Contents should be prepared on separate sheets.

Spelling should conform with "The Concise Oxford Dictionary"or "The Macquarie Dictionary" usage. The Système International d'Unites (SI) is to be used, with the abbreviations and symbols set out in Australian Standard AS1000.

All stratigraphic names must conform with the International Stratigraphic Guide and new names must first be cleared with the Central Register of Australian Stratigraphic Names, Australian Geological Survey Organisation, Canberra, ACT 2601, Australia. The Codes of Botanical and Zoological Nomenclature must also be adhered to as necessary.

The **Abstract** should be brief and informative.

Tables and Illustrations should be in the form and size intended for insertion in the master manuscript - 150 mm x 200 mm; column width 72 mm. If this is not readily possible then an indication of the required reduction (such as 'reduce to 1/2 size') must be clearly stated.

Maps, diagrams and graphs should generally not be larger than a single page. However, larger figures may be split and printed across two opposite pages.

The **Scale** of maps or diagrams *must* be given in bar form.

Half-tone illustrations (photographs) should be included *only* if essential and should be presented on glossy paper.

All Tables and Illustrations should be numbered serially with Arabic numerals and each must have a caption.

References are to be cited in the text by giving the author's name and year of publication. References in the Reference List should be listed alphabetically by author and then chronologically by date. Titles of journals should be cited in full - not abbreviated.

MASTER MANUSCRIPT FOR PRINTING

The journal is printed from master pages prepared by a desktop publishing computer program. When a paper has been accepted for publication, the author(s) will be supplied with a guide to acceptable electronic format for the submission of the revised manuscript. Galley proofs will be provided to authors for final checking prior to publication.

REPRINTS

An author who is a member of the Society will receive a number of reprints of his/her paper free. Authors who are not members of the Society may purchase reprints.

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ADDRESS - Royal Society of New South Wales,
PO Box 1525, Macquarie Centre, NSW 2113, Australia

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THE ROYAL SOCIETY OF NEW SOUTH WALES

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New England Rep.	*Vacant*
Southern Highlands Rep.	Mr R. Perry, BSc.

The Society originated in the year 1821 as the Philosophical Society of Australasia. Its main function is the promotion of Science by: publishing results of scientific investigations in its *Journal and Proceedings;* conducting monthly meetings; organising summer schools for senior secondary school students; awarding prizes and medals; and by liaison with other scientific societies. Special meetings are held for: the Pollock Memorial Lecture in Physics and Mathematics, the Liversidge Research Lecture in Chemistry, the Clarke Memorial Lecture in Geology, Zoology, and Botany, and the Poggendorf Lecture in Agricultural Science.

Membership, as an Ordinary, Absentee or Associate Member, is open to any person whose application is acceptable to the Society. An application must be supported by two members of the Society, one of whom personally knows the applicant. Subscriptions for the Journal only are accepted. The Society welcomes, from members and non-members, manuscripts of research and review articles in all branches of science, art, literature and philosophy for publication in the *Journal and Proceedings*. Manuscripts from non-members must be communicated through a member.

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The Contribution of Dwyer and Lions to the Design of Sexadentate Ligands

ANTHONY T. BAKER

ABSTRACT The series of papers published by Dwyer, Lions and their collaborators on metal complexes of sexadentate ligands represented one of the first attempts to design ligands which would yield metal complexes with particular structures. These papers are reviewed and their impact on contemporary and subsequent workers in coordination chemistry is assessed. Also included as Appendices are a supplement to complete the list of Dwyer's publications and some biographical notes on Dwyer and Lions. The collaboration of an organic chemist and a chemist from an analytical / inorganic background yielded important results for the field of coordination chemistry in the 1950s, a time when that field was developing rapidly. Dwyer and Lions have left a lasting impression on Australian coordination chemistry through their students and others adopting their approach of designing ligands to achieve particular structures for metal complexes.

INTRODUCTION

Sexadentate ligands are now well-known and ethylenediaminetetraacetic acid (EDTA) is commonly used in complexometric titrations and as an additive to many household products to sequester metal ions. Many structural motifs are possible for sexadentate ligands with Lions suggesting as many as 36 different structures (Lions, 1961). In his fascinating paper Lions anticipated the existence of macrocyclic sexadentate ligands and pendant arm macrocycles. Design and application of such ligand systems are now of strong interest. Among these relative newcomers in the area of multidentate ligands, the crown ethers and analogues are excellent examples. The crown ether 18-crown-6 (ie an 18-membered macrocycle with six oxygen donor atoms) is a well-known ligand of this class. In a review

Fig. 1. Francis Patrick John Dwyer

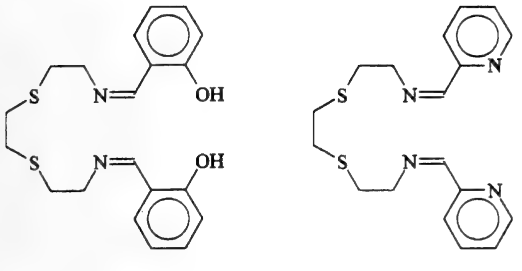
Fig. 2. Francis Lions (extreme right) at a meeting of the Sydney University Press Board (1965)

on ligand design, Lions' scheme of classification of ligands has been taken up (Black & Hartshorn, 1972-3) and some new structural motifs presented. In that review the ligands designed by Dwyer and Lions and subsequently by Lions and co-workers are extensively discussed.

An example of a linear sexadentate ligand, long-known but only recently studied in detail, is 2,2’:6’,2”:6”,2”’: 6”’,2””:6””,2”””-sexipyridine which is only just flexible enough to bind an extremely large metal ion through all donor atoms but has yielded binuclear double-helical metal complexes (Constable, 1994). Between the extremes of the linear sexadentates and the macrocyclic sexadentates lie a number of ligands with various branching patterns, with the branching occurring either at donor atoms or in the linking chains. Examples of the structures are three bidentate moieties bound to some structural base, which may be a single atom (see Fig. 11). Dwyer and Lions synthesised an example of this class, tris(2-pyridylmethyleneaminomethyl)-methane (Dwyer, Gill, Gyarfas & Lions, 1957), and a recent example is tris[3-(2’-pyridyl])pyrazol-1-yl]] hydroborat (Amoroso *et al.*, 1996). Another possible structure is that of two tridentate fragments linked by a short chain between the two central donor atoms (eg EDTA).

DWYER AND LIONS AND THEIR COLLABORATORS

Francis Patrick John Dwyer (Fig. 1) was well recognised in his own time and is perhaps best remembered for his work on sexadentate ligands and their metal complexes carried out in collaboration with Francis Lions (Fig. 2): "... Nyholm easily obtained an ICI Fellowship to study with Ingold in London in 1947. This was the same year that Dwyer accomplished the feat of preparing a sexadentate ligand as the highlight of his career" (Brock, 1992). The research program was undertaken because Dwyer realised that the metal complexes of linear sexadentate complexes



$\mathbf{H_2L^1}$ $\mathbf{L^2}$

Fig. 3. Linear sexadentate ligands.

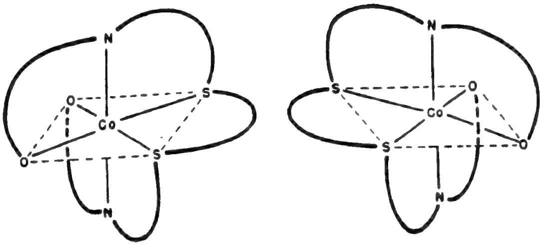


Fig. 4. The enantiomorphs of metal complexes of $\mathbf{L^1}$ and analogues.

may be chiral, depending on the conformation of the ligand in binding a metal ion, and these complexes when resolved may yield extremely high molecular rotations. The first ligand prepared was 1,8-bis(salicylideneamino)-3,6-dithiaoctane ($H_2\mathbf{L}^1$, Fig. 3) which binds metal ions after deprotonation of the hydroxyl groups (ie binding as $\mathbf{L}^1$) and the preparation of some Co(III) complexes was first reported briefly in a communication (Dwyer & Lions, 1947). Both the dextrorotatory and levorotatory forms were isolated and purified to giving opposite molecular rotations of 50,160° (Hg green line). The authors state (using I for $\mathbf{L}^1$ here): "Models show that I can function as a sexadentate chelate compound, occupying all six octahedrally disposed coördination positions about a six-covalent atom in one or other of two enantiomorphous strainless configurations provided that the nitrogen atoms are in *trans* positions and the sulfur atoms and oxygen atoms in *cis* positions to each other. The experimental evidence is wholly in favor of I being able to function as a sexadentate chelate compound."

Some time later a more substantial paper (Dwyer and Lions, 1950) was published in which the authors state that their motivation for the work was that: "The possibility that chelate compounds can be synthesised capable of attaching themselves to 6-covalent metallic atoms in such a way that each single chelate molecule occupies all six octahedrally disposed positions about one metal atom has been in the minds of many chemists for some considerable time, ...". As well as further details about complexes of $\mathbf{L}^1$, the first full paper includes information about the preparation of an analogous ligand from 2-hydroxy-1-naphthaldehyde and 1,8-diamino-3,6-dithiaoctane. The cobalt(III) complex of this ligand was resolved and the molecular rotations observed were −73,370° and +73,040°, higher values than observed for the cobalt(III) complex of $\mathbf{L}^1$. Dwyer and Lions mention that the previous 'record' (-47,610°) was held by Werner for tris(tetraamminedi-μ-hydroxocobalt (III))cobalt(III) salts (Werner, 1914). The authors argue that each pair of nitrogen and oxygen atoms must bond on the same plane and in order for the sulfur atom to maintain pyramidal coordination only a pair of enantiomorphs (shown schematically in Fig. 4) are possible. The paper concludes with a statement about the "tremendous molecular rotations which are higher than any previously recorded" for the metal complexes. It was mentioned in his obituary that Dwyer took great delight in a new

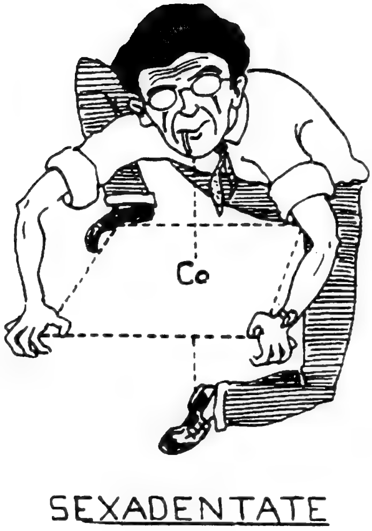
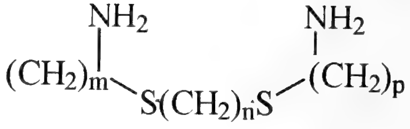


Fig. 5. Dwyer acting as a sexadentate ligand.



$$H_2N-(CH_2)_m-S(CH_2)_nS-(CH_2)_p-NH_2$$

Fig. 6. Diamines used in preparing analogues of $H_2\mathbf{L}^1$.

Code	m	n	p
EEE	2	2	2
TET	3	2	3
TTT	3	3	3
EET	2	2	3
ETT	2	3	3

specific rotation record (Sutherland, 1963).

Metal complexes of $\mathbf{L}^1$ and also $\mathbf{L}^2$ have recently been re-prepared and structurally characterised (Baker, Xiao, Craig & Baker, 1999). That work was carried out to confirm the sexadentate binding of the ligands, the mononuclear nature of the metal complexes and to further investigate the unusual magnetic moment originally reported for the iron(II) complex of $\mathbf{L}^1$ (Dwyer, Lions & Mellor, 1950).

There is a wonderful cartoon of Dwyer acting as a sexadentate ligand (Fig. 5), although it is noted that Dwyer is depicted as an EDTA-like ligand (Type 6 in Lions' classification) rather than a linear sexadentate ligand such as those Dwyer and Lions prepared (Type 1). This cartoon, drawn by Graham Hunt, a postgraduate student working with Dr Ian Ross, was presented as a farewell gift to Dwyer on departure from the University of Sydney for Canberra (Baker & Livingstone, 1985).

The next paper in the series is on the magnetic properties of the complexes with Mellor as an additional author (Dwyer, Lions & Mellor, 1950). Magnetic susceptibility data on the cobalt(III), cobalt(II), nickel(II) and iron(II) complexes of $\mathbf{L}^1$ and the cobalt(III) complex of bis-(β-hydroxy-α-naphthylideneamino)-3,6-dithiaoctane are reported. The diamagnetism of the cobalt(III) complexes indicated that the ligands were bound through all six donor atoms, since a tetrahedral complex would be paramagnetic. One interesting point is the unusual magnetic moment for the iron(II) complex of $\mathbf{L}^1$ of 3.22 BM, which is intermediate between the expected high-spin and low-spin values for octahedral d^6 complexes. This complex has been re-investigated recently and the magnetic moment at room temperature is normal for high-spin iron(II), though some spin-pairing is observed as liquid nitrogen temperature is approached (Baker, Xiao, Craig & Baker,1999).

A series of sulfur-containing α,ω-diamines with varying numbers of methylene groups between the heteroatoms were prepared and condensed with salicylaldehyde and 2-hydroxy-1-naphthaldehyde. The number of methylene groups between the heteroatoms were indicated by either E (ethylene) or T (trimethylene). In this system, the base used in the preparation of H_2L^1 and L^2 would be designated EEE (see Fig. 6). It was noted that the Schiff bases derived from diamines containing trimethylene groups would form complexes with six-membered chelate rings. The authors mentioned that Tschugaeff, in a series of papers published between 1908 and 1913, determined that the most stable complexes of dithioalkane derivatives occur when the two sulfur donor atoms are separated by an ethylene group. The existence of two series of isomeric cobalt(III) complexes of the Schiff bases derived from TET is noted (the 'green' and 'brown' salts). The authors commented that an optically active green salt yielded mainly the optically active brown salt, with some racemization noted. The explanation offered is that the nitrogen and sulfur donors remain bound in the transformation between the isomers but the oxygen donors exchange positions. TTT only yields a brown cobalt(III) complex and it is assumed that steric interactions preclude adoption of the meridional configuration (Dwyer, Gill, Gyarfas & Lions, 1952). The optically active forms of the bromide salt of the cobalt(III) complex of the Schiff base derived from 2-hydroxy-1-naphthaldehyde and TET gave molecular rotations of +87,030° and –84,200° (sodium D line): "So far as we are aware these are the highest ever recorded" .

The issue of the green and brown isomers has been taken up by one of Dwyer's students, Alan M. Sargeson FRS (recently retired from the Research School of Chemistry, Australian National University) in collaboration with crystallographers (Sargeson, White & Willis, 1976). The crystallographic studies were based on small amounts of original samples of the 'brown' and 'green' isomers of the cobalt(III) complexes of the Schiff base derived from TET, as the iodide salts. The cations of the 'brown' isomer were found to have the two sulfur donors in the same plane as the two nitrogen donors with the oxygen donors in the 'axial' positions, as had been suggested by others (Bosnich & Phillip, 1968). Interestingly, the recrystallised 'green' isomer was found to be optically inactive and to have two crystallographically independent cations one of which corresponded to that found in the 'brown' form and one which had the expected meridional configuration. This suggests that racemisation and isomerisation has occurred in the recrystallisation process (Sargeson, White & Willis, 1976).

A number of ligands analogous to H_2L^1 were reported in the fourth paper in the series. These ligands had been prepared by reacting 1,8-diamino-3.6-dithiaoctane (EEE) with 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-4-methoxybenzaldehyde, 2-hydroxy-5-methoxybenzaldehyde, 2-hydroxy-4-methylbenzaldehyde, 2-hydroxy-5-nitrobenzaldehyde and 2-hydroxy-5-bromobenzaldehyde, respectively. Cobalt (III) complexes of all these ligands were prepared. The iodide salt of the cobalt(III) complex of the Schiff base derived from EEE and 2-hydroxy-3-methoxybenzaldehyde was reported as giving high molecular rotations for the optically active forms (Collins, Dwyer & Lions, 1952).

The preparation of oxygen-containing analogues of H_2L^1 was reported in the fifth paper of the series (Dwyer, Gill, Gyarfas & Lions, 1953a). In one ligand (H_2L^3, Fig. 7), only one of the sulfur atoms in H_2L^1 was replaced by an oxygen atom and, in an-

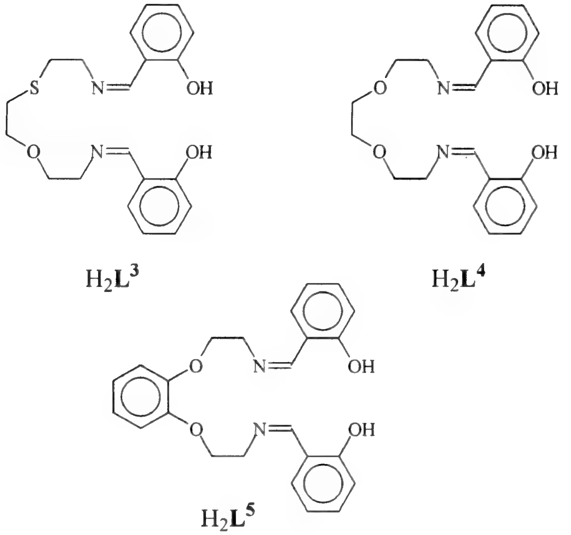


Fig. 7. Oxygen-containing analogues of H_2L^1.

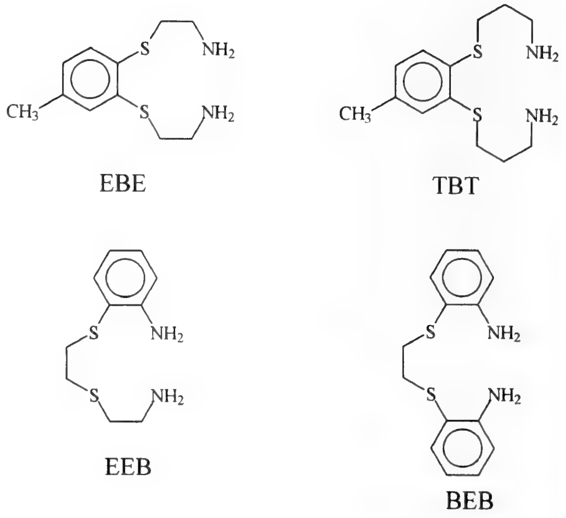


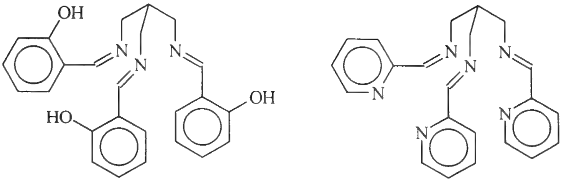
Fig. 8. 1,2-Phenylene-containing diamines used to prepare analogues of H_2L^1.

other (H_2L^4, Fig. 7), both sulfur atoms were replaced by oxygen atoms. Cobalt(III) complexes of the first ligand were prepared and resolved into the optical isomers but a Co(III) complex of the second ligand, though prepared successfully, was found to be unstable in solution. A further modification of the latter ligand was the introduction of a 1,2-phenylene group in place of the ethylene bridge between the oxygen atoms (H_2L^5, Fig. 7), though no stable cobalt(III) complex was isolated.

The sixth paper (Dwyer, Gill, Gyarfas & Lions, 1953b) revisits the work of the third paper (Dwyer, Gill, Gyarfas & Lions, 1952) but starts with the asymmetric EET and ETT diamines (Fig. 6). The bis-salicylidene derivatives of these diamines were prepared and cobalt(III) complexes were successfully isolated. It was found that the cobalt(III) complex of the Schiff base derived from the ETT diamine could be obtained in the green and brown forms. The brown form appeared unstable in solution and only the green form could be resolved successfully. The complex of the Schiff base of the EET diamine was found to exist only in the green form and could be successfully obtained in optically-active enantiomorphs.

Further introduction of *o*-phenylene groups into the diamines used to condense Schiff base derivatives were reported in the seventh paper (Dwyer, Gill, Gyarfas & Lions, 1954). Expanding their nomenclature scheme to include B for an *o*-phenylene moiety, the diamines prepared were EBE, TBT, EEB and BEB (Fig. 8). For EBE and TBT the *o*-phenylene moiety is derived from 3,4-dithioltoluene, so there is a methyl substituent on the aromatic ring which does not further extend the possibilities for isomers of the metal complexes (footnote, Dwyer, Gill, Gyarfas & Lions, 1954). With the EBE, BEB and TBT bases the bis-salicylidene derivatives were prepared but the bis-5-bromosalicylidene derivative of EEB was prepared. The cobalt(III) complexes of the bis-salicylidene derivatives of EBE and TBT were resolved into optical isomers. Attempts to resolve the cobalt(III) complexes of the Schiff base of BEB were unsuccessful. The cobalt(III) complex of the bis-5-bromo-salicyildene derivative of EEB was isolated as the iodide salt.

The last paper with both Dwyer and Lions as co-authors (Dwyer, Gill, Gyarfas & Lions, 1957) explores a suggestion made in the first paper (Dwyer & Lions, 1950) that the tris-salicylidene derivative of 2-aminomethyl-1,3-diaminopropane should be capable of acting as a sexadentate ligand (H_3L^6, Fig. 9). This Schiff base was prepared and the cobalt(III) and iron(III) complexes were isolated. An analogous ligand was prepared by reacting of 2-aminomethyl-1,3-diaminopropane with pyridine-2-aldehyde (L^7, Fig. 9). For this ligand only the iron(II) complex was prepared and it was noted that the ligand gives a discernible colour reaction with iron(II) in concentrations as low as 1 part in 5 million. This iron(II) complex is resistant to oxidation and even cerium(IV) does not yield the corresponding iron(III) compound. The authors were unable to resolve any of these complexes using the techniques employed at that time. The synthesis of 1,8-bis(2-pyridylmethyleneamino)-3,6-dithiaoctane (L^2, Fig. 3) and the preparation of several metal complexes were reported (Dwyer, Gill, Gyarfas & Lions, 1957). Optically active iron(II) cations were resolved as the iodide dihydrates. Cobalt(II) complexes were isolated but the cobalt(III) complex, obtained by cerium(IV) oxidation, was noted as "rather unstable". There is considerable discussion whether this ligand is actually functioning as a sexadentate ligand and comparing the results with those obtained for 1,8-bis(salicylideneamino)-3,6-diaza- octane (Das Sarma & Bailar, 1955). There has been recent confirmation that 1,8-bis(2-pyridylmethyleneamino)-3,6- dithiaoctane (L^2) functions as a sexadentate ligand, at least in the iron(II) and nickel(II) complexes (Baker, Xiao, Craig & Baker, 1999).



H_3L^6

L^7

Fig. 9. Tripodal ligands from 2-aminomethyl-1,3-diaminopropane.

Dwyer's views on nomenclature are legendary and included is a footnote (Dwyer, Gill, Gyarfas & Lions, 1957):

> the authors would draw attention to the lack of precision creeping into the nomenclature of multidentate chelate compounds. It is surely better to use words derived solely from Greek, or alternatively, Latin words. Words such as multidentate or polydontate, sexadentate or hexadontate, should be permissible, but bilingual hybrids such as polydentate or hexadentate should be avoided.

Dwyer would undoubtedly be appalled by the recent recommendations to change the terminology for ligands binding simultaneously through two donor atoms from the sonorous bidentate to didentate, though he probably would accept didontate. IUPAC also uses 'polydentate' extensively. This problem, certainly one in Dwyer's terms, arises because IUPAC appears to be only supporting the use of Greek numerical prefixes (Leigh *et al.*, 1998).

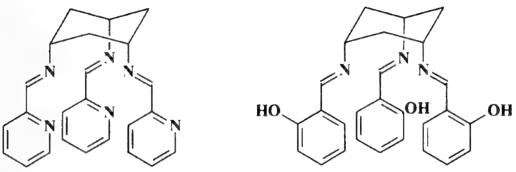
The work of Dwyer and Lions on sexadentate ligands had an immediate impact on the then fast-developing field of coordination chemistry in the 1950s. The work reported in the first two articles in the series is discussed in some detail in the influential book "Chemistry of the Metal Chelate Compounds" (Martell & Calvin, 1952). As well as discussing the complexes of L^1 and the analogous ligand derived from 2-hydroxy-1-naphthaldehyde, Martell and Calvin also note that Dwyer and Lions had already pointed out that the tris(salicylidene) derivative of 2-aminomethyl-1,3-diaminopropane should be able to act as a sexadentate ligand which Dwyer and Lions subsequently reported (Dwyer, Gill, Gyarfas & Lions, 1957).

Another major book on coordination chemistry in the 1950s was edited by John C. Bailar, Jr. and entitled 'The Chemistry of the Coordination Compounds'. Australian work, particularly of the 1940s and 1950s, is strongly referenced throughout the book, indicating that Australians were actively contributing to an emerging and rapidly expanding field. In the first chapter entitled General Survey, the work on the resolution of complexes of sexadentate ligands by Dwyer and Lions is mentioned (Bailar & Busch, 1956). The work is further mentioned in the discussion on chelate ring formation and reference to the papers in the series up to 1954 are given (Parry, 1956). Basolo in his chapter on six-coordinate complexes discusses the sexadentate work in some detail commenting that "this compound can only exist in one strainless geometrical form" (Basolo, 1956). However he includes a diagram (p. 287) that shows an incorrect conformation in that each ONS fragment of L^1 is shown coordinated to one face of the octahedron whereas Dwyer and Lions (Dwyer & Lions, 1950) argued that each ONS fragment must be bound meridionally (see Fig. 4). The detailed discussion of the research by Dwyer and Lions on metal complexes of sexadentate ligands indicates that the work was well received by the international community of coordination chemists almost immediately on publication.

That their work immediately inspired others to undertake similar projects is clear in that Das Sarma and Bailar reacted triethylenetetramine with 2 moles of salicylaldehyde to yield an analogue of H_2L^1 with an N_4O_2 donor set, rather than $S_2O_2N_2$ (Das Sarma & Bailar, 1954 and 1955).

An on-line and hard-copy search of the Science Citation Index reveals that Dwyer and Lions' work on sexadentate ligands continues to have an impact even 50 years after the publication of the initial communication. In the period 1974-97 authors made 90 references to the papers on the sexadentate ligands and their complexes in 65 papers. The most cited paper in that period was the first full paper (Dwyer & Lions, 1950) with 32 citations. Among the recent references was a review by Richard Keene, James Cook University of North Queensland, on polymetallic ligand bridged molecular assemblies (Keene, 1997). In a review of the developments in the stereochemistry of coordination compounds John C. Bailar, Jr., one of the most respected coordination chemists of all, credits Dwyer and Lions with initiating the study of sexadentate ligands (Bailar, 1981). He wrote in discussing the extremely high molecular rotations obtained for some of their complexes: 'Frank Lions wrote to me in his interesting Australian way, "I'm keen to reach 100,000". Unfortunately his untimely death put an end to the search.' Given that it was Dwyer who had the reputation for glorying in the molecular rotation records and it was he who suffered an untimely death it would appear that Bailar has confused the 'Franks'. Bailar also discusses the work on sexadentate ligands in his review on the stereochemistry of coordination compounds (Bailar, 1990).

Recent work on sexadentate ligands sim-



L^8 H_3L^9

Fig. 10. Sexadentate ligands based on a cyclohexane nucleus.

ilar to those investigated by Dwyer, Lions and co-workers has included some work on substituted salicylaldehyde derivatives of BEB and BTB diamines (Choudhury, Ray & Chakravorty, 1992) and some work on the cobalt(III) complexes of $\mathbf{L}^1$ (Chakraborty, Chandra & Chakravorty, 1994). Other elaborations on $\mathbf{L}^1$ include condensing EEE diamine with an aromatic aldehyde functionalised with a crown ether (Beer & Crane, 1988). In a study on sexadentate ligands, $H_2\mathbf{L}^1$ and several analogues have been synthesised (Rothin *et al.*, 1989). Substantial reference was made in that paper to the work of Dwyer and Lions.

Professor Stanley Kirschner, in an interview with A.B.P. Lever, has recently recounted an outstanding story about Dwyer (Lever, 1998). Kirschner was the principal organiser of the Sixth International Conference on Coordination Chemistry (VI ICCC) in Detroit in 1961. He applied for grant money from the US Air Force Office of Scientific Research to assist in bringing distinguished overseas scientists to the conference. The Air Force agreed to assist, not through providing airfares but by flying the overseas invitees to the United States as part of their Military Air Transport Service (MATS) program. According to Kirschner, Dwyer clearly enjoyed the experience (Lever, 1998):

> In order to fly these foreigners by MATS, they had to commission them in the US Air Force. I remember Professor Frank Dwyer (Australia) was commissioned a colonel in the US Air Force, in order to be flown from Australia to Detroit, which delighted him no end.

FURTHER WORK BY LIONS AND COLLABORATORS

In Sexadentate Chelate Compounds IX, Lions and Martin reported on an improvement in the synthesis of 1,3,5-triaminocyclohexane from phlorglucinol trioxime by employing the Birch reduction (ie sodium in liquid ammonia). The amine was subsequently reacted with pyridine-2-aldehyde (3 moles) or alternately salicylaldehyde to yield potentially sexadentate ligands ($\mathbf{L}^8$ and $H_3\mathbf{L}^9$, Fig. 10) (Lions & Martin, 1957). The pyridinyl ligand ($\mathbf{L}^8$) gave an intensely coloured iron(II) complex that could be oxidised by cerium(IV) to an unstable deep blue iron(III) complex. A cobalt(II) complex of this ligand ($\mathbf{L}^8$) was also obtained, that could be oxidised with great difficulty (H_2O_2 for a week) to a cobalt(III) complex. The intense colour of these complexes made resolution difficult and the almost colourless rhodium(III) complex was also prepared. However work ceased in this direction: "because of the inability of K.V.M. to continue with this work, we are unable to report its resolution." The cobalt(II) complex of $\mathbf{L}^9$ was formed which was found to oxidise readily to the cobalt(III) complex. The cobalt(III) complex of the ligand obtained by the reaction of the 1,3,5-triaminocyclohexane and 2-hydroxy-1-naphtaldehyde was also prepared.

The ligands reported in this ninth paper represent a radical departure from the linear sexadentate ligands reported in the original series of papers. Dwyer and Lions had been considering the preparation of tripodal sexadentate ligands as early as 1950 (Dwyer & Lions, 1950) and realised this intention in the eighth paper (Dwyer, Gill, Gyarfas & Lions, 1957).

In Sexadentate Chelate Compounds X (Lions & Martin, 1958), the authors refer to the introduction of the term "chelate" (Morgan & Drew, 1920) to correct a common error in terminology:

> The term "chelate compound" as used by the authors conforms to the original definition given by G.T. Morgan and H.D.K. Drew (*J. Chem. Soc*., **117**, 1457 (1920), footnote) in the words "The adjective "chelate" derived from the great claw or "chela" (chely) of the lobster and other crustaceans, is suggested for *these caliper-like groups* which function as two associating units to fasten on to the central metallic atom so as to produce heterocyclic rings." Some chemists today regard the actual final coördination compound as the chelate compound. In our opinion this is wrong. We would define a chelate compound as a compound "whose molecule is capable of attaching itself either directly or after loss of a proton or protons to a suitable metal atom at more than one point."

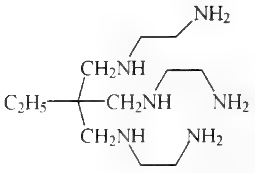
In introducing the term "chelate" Morgan and Drew cite ethylenediamine, propylenediamine and "αα-dipyridyl" as examples. The term chelate ring has subsequently been used to refer to the heterocyclic ring incorporating the metal atom (ion). In a biographical essay (Wardlaw and Drew, 1947) on Sir Gilbert Morgan it is mentioned:

> Incidentally Morgan introduced the very convenient term "chelate", now so widely used for rings containing coordinated links.

The point made by Lions and Martin is that the ligand is the "chelate" not the metal complex. Multidentate ligands are now often (correctly) referred to as "chelating agents" and the point is that a crab's claw is a claw whether it grasps something or not.

The tenth paper in the series reports on the preparation of a number of sexadentate ligands related to $H_2\mathbf{L}^1$ (Lions & Martin, 1958). The paper is particularly significant because it reports the preparation of the very important tridentate ligand pyridine-2-aldehyde-2'-pyridylhydrazone on which Lions and co-workers published substantially in the 1960s. The promise of this "reagent for the colorimetric estimation of cobalt" is noted in the Abstract of their paper.

The eleventh paper discusses the preparation of a tripodal ligand ($\mathbf{L}^{10}$, Fig. 11) from 1-bromo-2,2-bis(bromomethyl)-butane and ethylenediamine (Green, Catchpole, Phillip & Lions, 1963). This tripod ligand is structurally similar to the ligands based on a 1,3,5-triaminocyclohexane nucleus ($\mathbf{L}^8$ and $H_3\mathbf{L}^9$) in that three bidentate arms are attached to a supporting framework. Lions classified (Lions, 1961) the cyclohexane-based ligands separately (Type 18, whereas the tripodal ligands are Type 9) but in the later classification scheme no such distinction is made (Black & Hartshorn, 1972-3). This ligand ($\mathbf{L}^{10}$) was thought to act as a sexadentate ligand in cobalt(III)



$\mathbf{L}^{10}$

Fig. 11. A tripodal sexadentate ligand.

and nickel(II) as simple salts with appropriate physical properties could be isolated. The cobalt(III) complex was prepared by reacting sodium tris(carbonato)cobaltate(III) trihydrate with the ligand (**L**^{10}) in acid conditions. From a solution of **L**^{10} and cobalt(II) chloride in dilute hydrochloric acid that had been aerated it was possible to isolate a hygroscopic green solid. The colour and properties suggested that the compound "should be formulated as a *trans*-dichlorotetraminecobalt(III) salt" with one of the ethylenediamine arms uncoordinated and doubly protonated. Interaction of copper(II) with **L**^{10} (1:1 mole ratio) in ethanol yielded a purple complex in which only four nitrogen donor atoms were bound to the copper centre. When **L**^{10} (2 moles) coordinates to copper(II) (3 moles) in aqueous methanol a stable blue salt is formed that can be isolated as the sulfate, iodide or perchlorate. Conductivity measurements indicate that the complex cation carries a 6+ charge. Reaction of [Cu**L**^{10}]$^{2+}$ with sodium tris(carbonato)cobaltate(III) trihydrate yields a complex with one cobalt(III) centre and three copper(II) atoms. Conductivity measurements indicate that the complex cation carries the expected 9+ charge (Green, Catchpole, Phillip & Lions, 1963).

Further work has been carried out on analogues of **L**^{10}. The ligand abbreviated as sen has a methyl substituent at the 'head' of the tripod rather than the ethyl substituent in **L**^{10} and the ligand abbreviated as stn has propylenediamine 'legs' rather than the ethylenediamine 'legs' of **L**^{10} (Geue & Searle, 1983). It was noted that stn sometimes did not bind as a sexadentate ligand (Geue & Searle, 1983) as was observed for **L**^{10} in some cases (Green, Catchpole, Phillip & Lions, 1963). The straightforward preparation of a triamino tripodal ligand (tame) which is analogous to 2-aminomethyl-1,3-diaminopropane (Dwyer, Gill, Gyarfas & Lions, 1957) has also been reported (Geue & Searle, 1983).

CONCLUSION

Through their work on sexadentate ligands Dwyer and Lions demonstrated that it was possible to design ligands that would yield metal complexes with defined stereochemistries. It is clear that the significance of their contribution was recognised almost immediately by the community of coordination chemists. The importance of their contribution is still acknowledged over 50 years after their original publication. The synthesis of metal complexes of 'designed ligands' has been a continuing feature of Australian coordination chemistry, with the influence of Dwyer and Lions pervading much of the nation's significant contribution to this field of chemistry.

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(See Sutherland, 1963, for original list)

154	Coordination compounds as resolving agents.	*Nature (London),* **196**, 270 (1962 With B. Halpern
155	Mechanism of the inversion reaction between *d,cis*-dichlorobis(ethylenediamine)cobalt(III) ion and silver carbonate.	*J. Am. Chem. Soc.*, **85**, 1215 (1963) With A.M. Sargeson and I.K. Reid
156	Stereoscopic influences in metal complexes containing optically active ligands. VI. Oxalato-*l*-propylenediaminecobalt(III) complexes.	*J. Am. Chem. Soc.*, **85**, 661(1963) With T.E. MacDermott and A.M. Sargeson
157	The Preparation and Resolution of the bis-(2,2’-bipyridine)-1,10-phenanthrolinenickel(II) and the bis-(1,10-phenanthroline)- 2,2’-bipyridinenickel(II) ions.	*Aust. J. Chem.*, **15**, 453 (1962) With J.A. Broomhead
158	Resolution of racemic α-amino acids. I. Neutral α-amino acids.	*Aust. J. Chem.*, **16,** 510 (1963) With B. Halpern and K.R. Turnbull
159	Mechanisms of racemization of the 2,2’-bipyridinebis-(1,10-phenanthroline) nickel(II) ion and the 1,10-phenanthrolinebis-(2,2’-bipyridine)nickel(II) ion.	*Aust. J. Chem.,* **16**, 51 (1963) With J.A. Broomhead
160	Mono- and bis(2,2’-bipyridine) and (1,10-phenanthroline) chelates of ruthenium and osmium. I. Monochelates of bivalent, trivalent and quadrivalent ruthenium.	*Aust. J. Chem.*, **16**, 42 (1963) With H.A. Goodwin and E.C. Gyarfas
161	Stereospecific influences in metal complexes containing optically active ligands. VII. The isolation of the D- and L-isomers of bis((–)-propylenediamine)ethylenediaminecobalt(III) and bis(ethylenediamine)-(–)-propylenediaminecobalt(III) ions.	*J. Am. Chem. Soc.*, **85,** 2913 (1963) With T.E. MacDermott and A.M. Sargeson
162	Stereospecific influences in metal complexes containing optically active ligands. VIII. Isomerism of the cobalt(III) complex of the sexadentate *d,l*-4-methyl-1,8-bis(salicylidenamino)-3,6-dithiaoctane.	*J. Am. Chem. Soc.*, **85**, 2916 (1963) With T.E. MacDermott
163	Mono- and bis- (2,2’-bipyridine) and (1,10-phenanthroline) chelates of ruthenium and osmium. II. Bis chelates of bivalent and trivalent ruthenium.	*Aust. J. Chem.*, **16,** 544 (1963) With H.A. Goodwin and E.C. Gyarfas

164	Stereospecific preparation of L-carbonataobis (*l*-propylenediamine)cobalt(III) iodide.	*Inorg. Chem.*, **2**, 871 (1963) With T.E. MacDermott
165	Resolution of DL-α-amino acids. II. Acidic α-amino acids.	*Aust J. Chem.*, **16**, 727 (1963) With B. Halpern and K.R. Turnbull
166	Disproportionation in synthetic reactions with cobalt(III) complexes.	*Aust. J. Chem.*, **16**, 921 (1963) With D.A. Buckingham and A.M. Sargeson
167	Chelating Agents and Metal Chelates.	Academic Press, New York, 1964. Editor, with D.P. Mellor
168	Enzyme-metal ion activation phenomena with metal complexes.	In Chelating Agents and Metal Chelates, p 335 ff
169	Metal chelates in biological systems.	In Chelating Agents and Metal Chelates , p 383 ff With A. Shulman
170	Stereospecific influences in metal complexes containing optically active ligands. IX. The equilibrium ratios and isolation of some of the isomers in the mixture tris((±)-propylenediamine)cobalt(III) chloride.	*J. Am. Chem. Soc.*, **86**, 590 (1964) With A.M. Sargeson and L.B. James
171	Mono and bis(2,2'-bipyridine) and (1,10-phenanthroline) chelates of ruthenium and osmium. III. Monochelates of bivalent, trivalent and quadrivalent osmium.	*Aust. J. Chem.*, **17**, 315 (1964) With D.A. Buckingham, H.A. Goodwin and A.M. Sargeson
172	Mono and bis(2,2'-bipyridine) and (1,10-phenanthroline) chelates of ruthenium and osmium. IV. Bis chelates of bivalent and trivalent osmium.	*Aust. J. Chem.*, **17**, 325 (1964) With H.A. Goodwin and A.M. Sargeson
173	Mono and bis(2,2'-bipyridine) and (1,10-phenanthroline) chelates of ruthenium and osmium. V. Mixed 2,2'-bipyridine and 2,2',2"-terpyridine chelates of bivalent and trivalent osmium.	*Aust. J. Chem.*, **17**, 622 (1964) With D.A. Buckingham and A.M. Sargeson
174	Metal complexes with heterogeneous ligands.	Australian Patent 251, 582 (1964) ANU (by FPJD, R.D. Wright and A. Shulman)
175	Preparation of new phenanthroline and bipyridine derivatives.	Australian Patent 251, 598 (1964) ANU (by FPJD, R.D. Wright and A. Shulman)
176	Inhibition of Landschuetz ascites tumor growth by metal chelates derived from 3,4,7,8-tetramethyl-1,10-phenanthroline.	*Brit. J. Cancer*, **19**, 195 (1965) With E. Mayhew, E.M.F. Roe and A. Shulman

177	Circular dichroism and rotary dispersion of Co(III) oxalato-glycinato complexes.	*Aust. J. Chem.*, **18**, 1919 (1965) With I.K. Reid and A.M. Sargeson
178	Osmium(III)-osmium(II) electrode potentials The effects of charge, conjugation, coordinated halide, and substitution in the ligand.	*Inorg. Chem.*, **5**, 1243 (1966). With D.A. Buckingham and A.M. Sargeson
179	Mixed bidentate and tridentate complexes of cobalt.	*Aust. J. Chem.*, **19**, 2045 (1966) With B. Bosnich
180	The rates of solvent aquation of a series of halogenocobalt(III) complexes.	*Aust. J. Chem.*, **19**, 2051 (1966) With B. Bosnich
181	The rate of exchange of propylenediamine-tetraacetic acid with its cadmium complex.	*Aust. J. Chem.*, **19**, 2213 (1966) With B. Bosnich and A.M. Sargeson
182	Bis-1,10-phenanthroline complexes of divalent ruthenium.	*Aust. J. Chem.*, **19**, 2229 (1966) With B. Bosnich
183	The mechanisms and steric course of substitution at a divalent ruthenium center.	*Aust. J. Chem.*, **19**, 2235 (1966) With B. Bosnich
184	Iron diol complexes of substituted phenanthrolines.	US Patent 3,329,681 (1967) ANU (by FPJD (Lola M. Dwyer, executrix), R.D. Wright and A. Shulman)
185	Quaternary ammonium salts of substituted phenanthrolines.	US Patent 3,338,906 (1967) ANU (by FPJD (Lola M. Dwyer, executrix), R.D. Wright and A. Shulman)
186	Potassium µ-oxo-bis[pentachlororuthenate(IV)] 1-hydrate.	*Inorg. Synth.*, **11**, 70 (1968) With J.A. Broomhead, H.A.Goodwin, L. Kane-Maguire and I. Reid
187	Quaternary ammonium salts of substituted phenanthrolines as bactericides and fungicides.	US Patent 3,499,966 (1970) [Division of US Patent 3,338,906] With R.D. Wright and A. Shulman

APPENDIX 2: BIOGRAPHICAL NOTES FOR DWYER AND LIONS

Francis Patrick John Dwyer was born at Nelson Plains NSW on December 3, 1910. He gained secondary education at Marist Brothers College, Maitland. At the University of Sydney he graduated BSc in 1930 and MSc with First Class Honours in 1933. He was awarded the DSc degree (1945) for a thesis entitled 'The diazoamino compounds and their metallic salts and metallic hydroxide lakes'. This was the first DSc in chemistry for nearly 20 years. He held the post of Head Teacher of Inorganic Chemistry at Sydney Technical College from 1934-46. He was then appointed to the staff of the University of Sydney as a Senior Lecturer. In 1954 he visited Northwestern University and was George Fisher Baker lecturer at Cornell University. He was offered posts in the USA and in an effort to keep him in Australia he was appointed Reader at the John Curtin School of Medical Research at ANU and was promoted to Professor in 1960. He joined the Fellowship of the Australian Academy of Science in 1961 and died on June 22, 1962.

Dwyer was an extremely productive and renowned coordination chemist of the so-called 'Sydney School' which properly traces its heritage form pioneering work carried out in the 1910s by E.E. Turner and G.J. Burrows at the University of Sydney. Much of the output of the 'Sydney School' was published in the *Journal and Proceedings of the Royal Society of New South Wales* and many of Dwyer's papers were published there also. Dwyer's early researches as an Honours and postgraduate student were on aromatic nitrosations and x-ray crystallography, respectively, but he soon came to coordination chemistry. His work with D.P. Mellor on oxime complexes of palladium was published in the *Journal and Proceedings of the Royal Society of New South Wales* and the *Journal of the American Chemical Society*. Of subsequent publications in the *Journal and Proceedings of the Royal Society of New South Wales*, the vast majority was co-authored with R.S. Nyholm. Nyholm was President of the Royal Society of New South Wales for 1954-5 and has the unusual distinction of having his Presidential Address delivered *in absentia*. He had already departed to take up a Chair at University College, London and his address was presented by D.P. Mellor. Nyholm later became President of the Chemical Society and had a pivotal role in the amalgamation of that Society with the Royal Institute of Chemistry and other smaller societies. Dwyer was also active in the Royal Society of New South Wales, serving on Council.

Francis Lions was born in Perth on November 30, 1901. He graduated from the University of Sydney with First Class Honours and the University Medal in Chemistry in 1923. He completed PhD studies in Manchester working under Sir Robert Robinson. In 1925-6 he held post-doctoral positions at Oxford with W.H. Perkin, jnr and at University of Graz with Professor Pregl. He returned to University of Sydney as a Lecturer in 1926 and was promoted to Reader in 1947. He was President of the Royal Society of New South Wales in 1946. His Presidential Address was entitled "Freedom of Science" and was inspired by his visit to the USA, as the representative of the Royal Society of New South Wales, at the expense of the National Academy of Science, Washington and the American Philosophical Society, Philadelphia. These learned societies held discussions on the future of science with representatives of many national scientific societies. He was a Fellow of the Senate of the University of Sydney for a decade (1949-59). He was awarded the Royal Society of New South Wales's Medal in 1965. He delivered the Dwyer Memorial Lecture of the University of New South Wales Chemical Society in July, 1968. He retired from the University of Sydney in 1966 and died in March, 1972.

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Origins of the Continental Crust

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Abstract The genesis of the continental crust is a first-order geological and geochemical problem. The marked enrichment of a number of elements such as Cs and Rb (by ~100 fold) in the continental crust compared with estimates of primitive mantle abundances, is matched by complementary depletions in the global mantle source regions tapped by mid-ocean ridge basalts. The "depleted mantle" source of the most abundant crustal rock type (oceanic) represents a residue from continental crust extraction. At least 60% of the mantle has been involved in formation of the continental crust, and maybe all has been affected to some degree by mixing either with residues from crustal formation or with deeply recycled continent-derived sediments. There is a strong geochemical argument that any depleted ("refractory") mantle component of the continental lithosphere can only represent a small fraction of the total mantle involved in continental crust formation. There can be no enduring retention of residual mantle in any vertical, continental crust-mantle differentiation process; vertical juxtaposition may likely represent a fortuitous linkage of buoyant crust and mantle.

The dioritic-to-tonalitic major element composition of the continental crust can only be formed via a 2-stage process from the upper mantle: a first stage of basalt (or high-Mg andesite) formation; and a second stage (or more) of differentiation of this protolith. The second stage typically involves H_2O as a critical component through: 1. fractional crystallisation of basalt; 2. direct melting of subducted/ underplated mafic lithosphere; 3. fractionation of high-Mg andesites generated by wet melting of peridotite. A major constraint on all models of continental crustal genesis is the necessity of residue (1st stage depleted mantle; 2nd stage cumulates or restite) disposal. Mass balance indicates the MORB source represents the former, but the location of the latter for Late Proterozoic to Phanerozoic crust is problematic. In detail, it is clear that much of the crust, while produced initially in the Archean and early Proterozoic, has been subjected to considerable intra-crustal recycling. Island arc magmas alone of the common terrestrial magma types are characterised by elevated (and strongly fractionated) Pb/Ce and U/Nb that are also distinctive of the continental crust.

Reasonably well-constrained estimates of the magmatic flux in present-day intra-oceanic arcs are 80 to 200 $km^3\ km^{-1}$ arc strike length $m.y.^{-1}$, equivalent to a global crustal production rate of ~3 to 7 $km^3\ a^{-1}$. These fluxes can be compared with an incremental linear survival rate for continental crust over 4 billion years of ~1.6 $km^3\ a^{-1}$, and a present-day subducted sediment flux of 1 $km^3\ a^{-1}$. If arc magmas are not involved in continental crustal genesis, then a considerably larger subducted sediment flux is needed to dispose of the surplus crust produced in supra-subduction zone environments. Detailed consideration of the best-studied intra-oceanic arc crustal structure (Izu–Bonin) suggests a considerable tonalite fraction and a bulk composition equivalent to mafic andesite. Accumulation sub-Moho of olivine–clinopyroxene-rich cumulates and their incorporation into the advecting mantle wedge and recycling deep into the mantle is advocated. In essence this hypothesis constitutes a revival of S.R. Taylor's (1967) "andesite model" for the origin of the continental crust.

Temporal changes in continental crust genesis through Earth history have nevertheless been important. Partial melts of subducted and hydrated mafic lithosphere were significant juvenile crustal constituents in the Archean. Mantle wedge melting triggered by slab-derived (through dehydration) fluids has been significant from at least the Proterozoic onwards. Post-Proterozoic constraints on continental crustal growth are: **1.** without deep recycling of H_2O, neither melting of a subducted slab nor overlying mantle wedge occurs. Furthermore, the order of crystalline phase appearance in cooling basalt magmas containing a few % H_2O is: olivine, pyroxene, plagioclase – the delay in plagioclase appearance in the "wet basalt case" enhances concentration of Si, Al, Na, and K in residual magmas (key elements present in abundance in granites). The presence of hydrated minerals (amphibole/biotite) in crystallisation products of wet magmas is also important in generation of granitic magmas during ultra-metamorphism of continental crust. **2.** a key requirement for fractional crystallisation is for the system to "be left alone" (i.e., allowed to cool and crystallise) with minimal accompanying magma chamber tapping or replenishment. Neglect is a function of local magma flux, and in arcs, this is ~0.1 to 0.3 of the mid-ocean ridge flux. **3.** disposal of ultramafic/mafic crystalline cumulates from basalt fractionation processes is crucial for production of granodioritic crust. Cumulates may be underplated (sub-Moho) as part of the continental lithosphere or dynamically removed. Melts escaping from a supra-subduction zone system are not coupled to crystal cumulates and residual mantle; the latter are advectively dragged by the subducted lithosphere and recycled deep into the mantle. A summary of this Phanerozoic style of growth would emphasise "damp, neglect, and waste disposal" as crucial factors.

INTRODUCTION

The composition and development of the quartzofeldspathic continental crust appear to be unique features of the Earth among the terrestrial planets. This stands in contrast with the ubiquity of basaltic crust, which is widespread on Mercury, Venus, Mars, and planetesimals such as the eucrite (asteroidal) parent bodies, and dominates ~70% of the Earth's solid surface. A restricted planetary occurrence of quartzofeldspathic crust limits our perspective of the possible constraints on the genesis and development of the continents, and in overall terrestrial planet terms, the continental crust can be dismissed as volumetrically insignificant. However, in addition to its intrinsic importance as a buoyant, albeit rocky life raft for *homo sapiens*, extraction of the continental crust from the mantle has had profound geochemical consequences for the planet as a whole. Thus the genesis of the continental crust is a first-order geological and geochemical problem, and we are a long way from fully understanding its origins.

In my experience, explaining the genesis of the continental crust to first-year undergraduate Earth science students is one of the more challenging educational tasks because of: 1. the complexity of the petrogenetic processes required for fractionation, ultimately, of quartzofeldspathic compositions from a

Table 1. Comparisons of estimates of bulk Continental Crust compositions

wt.%	RF 95	TM 95	W 95	RF lower	RF middle	RF upper
SiO2	59.1	56.2	61.5	52.3	60.6	66
TiO2	0.7	0.9	0.7	0.8	0.7	0.5
A1203	15.8	15.9	15.1	16.6	15.5	15.2
FeO*	6.6	9.1	7	8.4	6.4	4.5
MnO	0.11	0.18	0.1	0.1	0.1	0.1
Mgo	4.4	5.3	3.7	7.1	3.4	2.2
Cao	6.4	7.4	5.5	9.4	5.1	4.2
Na20	3.2	3.1	3.2	2.6	3.2	3.9
K20	1.9	1.1	2.4	0.6	2.01	3.4
P205	0.2	0.16	0.18	0.1	0.1	0.4
pprn						
Li	11	13	18	6	7	20
Sc	22	30	16	31	22	11
V	131	230	98	196	118	60
Cr	119	185	126	215	83	35
CO	25	29	24	38	25	10
Ni	51	105	56	88	33	20
Cu	24	75	25	26	20	25
Zn	73	80	65	78	70	71
Ga	16	18	15	13	17	17
Rb	58	32	78	11	62	112
Sr	325	260	333	348	281	350
Y	20	20	24	16	22	22
Zr	123	100	203	68	125	190
Nb	12	11	19	5	8	25
Cs	2.6	1	3.4	0.3	2.4	5.6
Ba	390	250	584	259	402	550
La	18	16	30	8	17	30
Ce	42	33	60	20	45	64
Pr	5	3.9	6.7	2.6	5.8	7.1
Nd	20	16	27	11	24	26
Sm	3.9	3.5	5.3	2.8	4.4	4.5
Eu	1.2	1.1	1.3	1.1	1.5	0.9
Gd	3.6	3,3	4	3.1	4	3.8
Tb	0.56	0.6	0.65	0.48	0.58	0.64
Dy	3.5	3.7	3.8	3.1	3.8	3.5
Ho	0.76	0.78	0.8	0.68	0.82	0.8
Er	2.2	2.2	2.1	1.9	2.3	2.3
Yb	2	2.2	2	1.5	2.3	2.2
Lu	0.33	0.3	0.35	0.25	0.41	0.32
Hf	3.7	3	4.9	1.9	4	5.8
Ta	1.1	1	1.1	0.6	0.6	2.2
Pb	12.6	8	14.8	4.2	15.3	20
Th	5.6	3.5	8.5	1.2	6.1	10.7
U	1.4	0.91	1.7	0.2	1.6	2.8

Abbreviations: RF 95 = Rudnick and Fountain (1995); TM 95 = Taylor and McLennan (1995); W 95 = Wedepohl (1995); RF lower, middle, and upper are Rudnick and Fountain (1995) estimates for lower, middle and upper continental crust respectively.

primary ultramafic (mantle) lithology; 2. our relatively poor knowledge of the lowermost continental crust; 3. the significance and global equivalence of the Moho – the seismically-recognised boundary between crust and mantle; 4. the strong likelihood of secular changes in production processes; 5. our poor grasp of present-day mass fluxes (both in and out of the mantle) at convergent plate margins where current continental crust production is developed; 6. the possibility that production of continental crust is significantly non-linear through time, with major pulses of activity superimposed on an overall peak production (or survival) interval straddling the Archean–Proterozoic boundary.

In this paper, I present a summary of our current understanding of the bulk composition of the continental crust including possible stratification and heterogeneities, examine the various processes that have been proposed to account for this composition, discuss the present-day mass fluxes at convergent margins, and finally, explore the necessity (and implications) for recycling the complementary residues of crust formation.

COMPOSITION OF THE CONTINENTAL CRUST AND IMPLICATIONS

We have some understanding of the bulk composition of the crust after decades of effort and a variety of chemical and physical approaches. Recent reviews that include discussions of the various geological, geochemical, and geophysical approaches that can be deployed to derive compositional estimates have been presented by Rudnick (1995), Rudnick and Fountain (1995), Taylor and McLennan (1995; 1997), and Wedepohl (1995). A granodioritic bulk upper (< 15 km depth) continental crustal composition (~66 wt.% SiO_2) has been relatively straightforwardly established (for summaries, see Table 1, and the Geochemical Earth Reference Model web site: (http://www-ep.es.llnl.gov/germ/germ-home.html) through a combination of brute force grid sampling, deep continental drilling, or by analysis of crustal-derived sediments formed via large-scale natural processes such as glacial (moraines) and peri-glacial (e.g. loess) activity (see Taylor and McLennan, 1985).

In the case of the intermediate and deeper crust, we share the general problem of lack of exposure that students of the uppermost mantle face even more acutely. For the intermediate crust, we can locate areally extensive terranes, now exposed at the Earth's surface, that acquired their mineralogical and chemical characteristics through tectonic cycling at pressures matching those normally characteristic of the middle to lower crust in the ~0.5 to 1 GPa range. And for the lowermost crust, reliance has been placed on a few areally extensive exposures of apparent continental crust-upper mantle straddling sections (Salisbury and Fountain, 1988) such as the Ivrea Zone in northern Italy, or the Horoman Complex in Hokkaido, coupled with suites of xenoliths brought to the surface in explosive volcanic eruptions. Critical additional constraints are velocity-density profiles acquired through analysis of seismic waves transmitted through the crust (Mooney and Brocher, 1987; Holbrook *et al.*, 1992), and measurements of (near) surface heat flow. Inevitably, these latter techniques are integrative over much larger volumes of crust than by the geochemical analysis of individual rock samples.

A consensus (see Rudnick and Fountain, 1995) seems to have been reached that:

1. Overall, the continental crust is chemically and lithologically stratified below

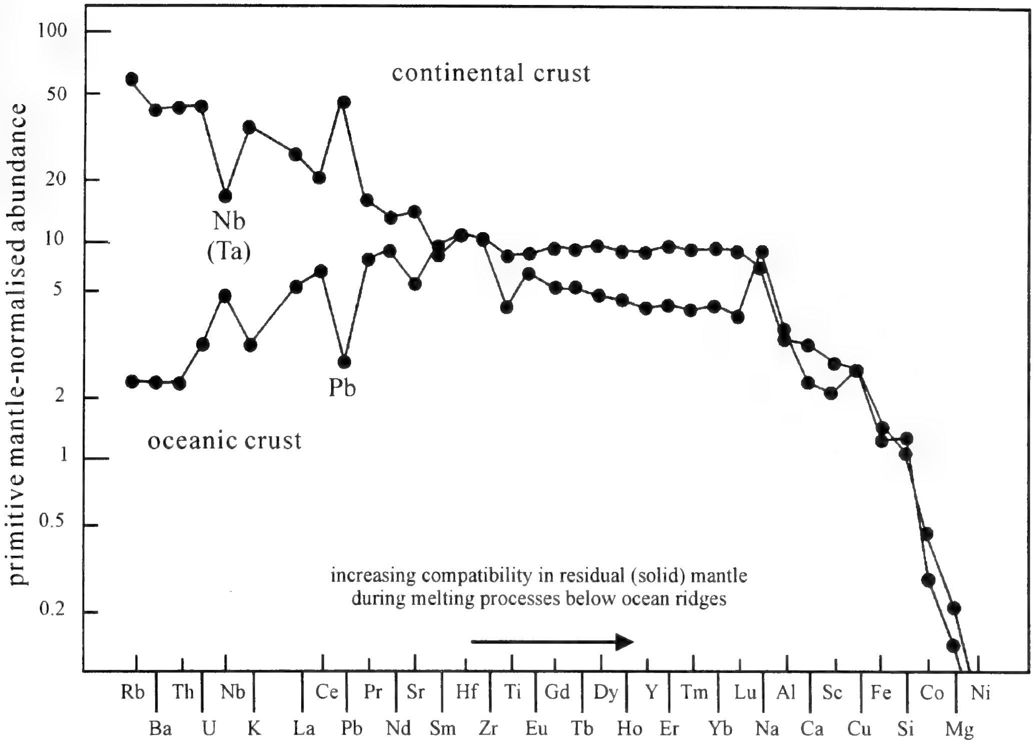

Fig. 1. Comparison of primitive mantle (equivalent to bulk silicate Earth)-normalised elemental abundances in the continental and oceanic crust after Hofmann (1988).

a felsic uppermost crust (compressional seismic wave velocity [V_p] = ~6.2 km s^{-1});

2. the middle crust (~15 to 25 km depth) is lithologically heterogeneous, of amphibolite facies mineralogy, and intermediate (~60 wt.% SiO_2 , 3.5 wt. MgO) in terms of bulk composition (V_p = 6.2 to 6.5 km s^{-1}) ;
3. the lowermost crust (~25 to 40 km depth), is also lithologically heterogeneous, overall of mafic granulite facies mineralogy (comprising predominantly aluminous pyroxenes and plagioclase feldspar) and broadly of basaltic (~52 wt % SiO_2, 7 wt. MgO) composition(V_p = 6.9 to 7.2 km s^{-1}) (Table 1).

We need, of course, to address further the problem of the origins of chemical stratification of the continental crust, but it is also instructive to examine the overall fractionation (relative enrichments/depletions) of trace elements between the crust (both continental and oceanic) and mantle. Hofmann (1988) presented a comprehensive review of elemental fractionation patterns in the silicate portion of the Earth, and despite subsequent minor adjustments to estimates of specific trace element abundances, his primary conclusions remain valid:

1. the average bulk compositions of continental and oceanic crusts form complementary abundance patterns (Fig. 1);

2. for the continental crust, the maximum elemental enrichments relative to best estimates of primitive mantle (i.e., bulk silicate Earth) values are 50- to 100-fold, and are attained by the most incompatible (in major mantle-forming silicate/oxide minerals) elements (Cs, Rb, Ba, and Th);
3. for the oceanic crust, maximum enrichments (10-fold) are attained by moderately incompatible elements (Na, Ti, Zr, Hf, Y, and the intermediate to heavy lanthanides);
4. these relationships can simply be accounted for via a 2-stage model of firstly extracting continental and subsequently oceanic crust from an initially primitive mantle. In other words, the "depleted mantle" source of the most abundant crustal rock type (oceanic) represents a residue from prior continental crust extraction.

Generally, the trace element abundance pattern of the continental crust requires (at some genetic stage): (1) low % of mantle melting, or a 2-stage process in which a low % partial melt is important in one of the stages; (2) garnet-bearing protolith involvement; (3) fluid/solid elemental fractionation to account for the marked enrichment of Pb compared with other trace elements of similar melt/solid incompatibility.

Crucial additional points can be made concerning the mass balance between continental crust and mantle, particularly with respect to the amount of the mantle that must have been involved in continent formation. For example, given that the mass of the continental crust is ~0.6% of the mantle, an overall 100-fold enrichment in a trace element such as Cs compared with the primitive mantle, requires (minimally) that all of the Cs in ~60% of the mantle has been transferred to the continental crust by one or more processes. Alternatively, all of the mantle may have been depleted in Cs to a somewhat lesser extent. Tracking enrichments in the continental crust of specific elements relative to the mantle can also be achieved (e.g. Allègre, 1997) through a simultaneous solution of time-integrated mass balances of the radioactive parent – stable daughter pairs of $^{87}Rb \rightarrow ^{87}Sr$, $^{238}U \rightarrow ^{206}Pb$, $^{235}U \rightarrow ^{207}Pb$, $^{232}Th \rightarrow ^{208}Pb$, $^{147}Sm \rightarrow ^{143}Nd$, and $^{176}Lu \rightarrow ^{176}Hf$. Utilising this approach, a minimum of 50% of the mantle must have been involved in formation of the continental crust.

Noting that the upper mantle (above the Transition Zone at ~700 km depth) is volumetrically ~35% of the entire mantle, the formation of the continental crust requires complete extraction of incompatible elements from a mantle source that exceeds the volume of the upper mantle alone. We can conclude from these simple calculations that at least some portion of the lower mantle has been involved in continental crustal formation. The possibility further exists that all of the mantle has been chemically fractionated to a varying extent by this major process. Note the further point that the depleted mantle source regions of MORB exceed volumetrically that of the upper mantle alone; models of 2-layered mantle convection that identify the separately convecting upper and lower mantle with depleted and fertile (or primitive) compositions respectively, are too simple.

Various other lines of geochemical and geophysical evidence exist that support the probabilities that:

1. penetration of subducted oceanic lithosphere through the Transition Zone into the Lower Mantle requires a return mass flow from Lower to Upper Mantle, ultimately rendering continental crustal extraction from deeply-derived mantle more likely (Creager and Jor-

dan, 1984; Van der Hilst and Seno, 1993);

2. abundances and isotopic systematics of the noble gases are consistent with marked variability in the degree of degassing of the mantle. We assume that mantle degassing is fundamentally linked with melting of the mantle, leading at low pressures to gas bubble exsolution and escape, accompanied by hydrothermal stripping of gases from crustal rocks. The continuing flux of ^{3}He from the mantle (a non-radiogenic, primordially-trapped gaseous element that is lost to space once degassed from the Earth's interior) requires the isolation of some of the mantle throughout the age of the Earth from these processes (e.g. Hart *et al.*, 1992; Hanan and Graham, 1996) Furthermore, it appears on the basis of Ne (Honda *et al.*, 1993), Ar, and Xe (e.g. Allègre *et al.*, 1996; Hofmann, 1997) that a primordial solar (rather than so-called planetary) noble gas component still resides in the mantle, and that the source regions of mid-ocean ridge basalts (MORB) have been more extensively degassed than those of ocean island basalts (OIB) or hot spots/mantle plumes;
3. no portion of the mantle still preserves chondritic values of (refractory) elements that are commonly accepted to have been accreted in chondritic relative proportions; this conclusion derives from the fact that no significant plume source (and certainly not the MORB source) has present-day chondritic ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf (Hofmann, 1997; Vervoort *et al.*, 1999). Furthermore, if the Lower Mantle is represented by an isotopic end-member recognised in OIB mixing arrays (variously termed FOZO or C – see Hart *et al.*, 1992; Hanan and Graham, 1996), then the elevated ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf of this component is clearly inconsistent with a chondritic source. Thus it can be argued that all of the mantle has directly experienced one or more episodes of melt extraction and/or been subjected to mixing with fractionated components (e.g. oceanic lithosphere plus entrained sediments).

CONTINENTAL CRUST MANUFACTURE – THE GRANITE PROBLEM

It is possible to obtain 100-fold enrichments of highly incompatible (i.e., bulk distribution coefficient [D = concentration of element in residual crystalline phases / concentration of element in the melt phase] <<1) trace elements such as Cs in a melt phase by ≤1% partial melting of primitive mantle material. However, the host quartzofeldspathic mineralogy of the upper continental crust cannot be reconciled with such a simple, single stage melting process. There is no experimental or theoretical basis for invoking a single melting stage production of granodioritic upper continental crust with ~66 wt. SiO_2 directly from the mantle. Rather, it has long been recognised that a minimum of two stages is required for creation of granodiorite from a peridotitic (upper mantle) lithology — a first stage of basalt or high-Mg andesite production followed by an intracrustal melting stage, possibly accompanied by other non-igneous processes (e.g. Albarède and Michard, 1986; Arculus and Ruff, 1990). It has also been clear that understanding the origins of granite (*sensu lato*) is fundamental to unravelling the process of continental crust formation (e.g. Tuttle and Bowen, 1958; White and Chappell, 1977; Campbell and Taylor, 1985). Thus, in contrast to formation of the predominantly basaltic oceanic crust, which can theoretically be produced in a single-stage melting of the mantle combined with upward melt transport, manufacture of the continental crust clearly involves a more complex genesis.

We have considerable field, laboratory (both analytical and experimental) and theoretical evidence that granitic compositions can be generated through two major processes:

1. Fractional crystallisation of a more mafic parental melt – in the case where the parental melt is basaltic, we know that the volume of granitic melt that can be produced is ~≥10% of the original volume of the parent. The somewhat acrimonious debate that occurred between N.L. Bowen and C.N. Fenner earlier this century concerning the compositional trends generated by fractional crystallisation of basaltic magma, argued from experimental and observational evidence respectively (see Bowen, 1928), has in fact been resolved through subsequent recognition of the importance of dissolved volatiles. For example, a critical requirement for the generation of significant amounts of granitic melts through fractional crystallisation, is the presence of dissolved H_2O. We know that a major effect of several % dissolved H_2O in a mafic melt is to retard the crystallisation of feldspar (and quartz) relative to anhydrous and hydrous ferromagnesian minerals (olivine/pyroxene and amphibole, respectively). Early nucleation of plagioclase feldspar together with olivine and pyroxene in relatively anhydrous, tholeiitic MORB suites, results in trends of marked Fe-enrichment at specific SiO_2 contents compared with hydrous fractional crystallisation conditions, and production of trivial amounts of granitic residual melt.
2. Partial melting of a variety of mafic–through intermediate SiO_2–to felsic lithologies, particularly those that contain hydrous minerals (e.g. Clemens and Vielzeuf, 1987; Wyllie, 1992). For example, the coincidence of natural granitic compositions of the Lachlan Fold Belt of eastern Australia, generated by partial melting of precursor crustal lithologies (Chappell, 1998) with the experimentally- determined (Tuttle and Bowen, 1958) solidus minimum in the system $NaAlSi_3O_8 - KAlSi_3O_8 - SiO_2 - H_2O$ is unequivocal proof of the importance of hydrous partial melting of crust in granite genesis. Partial melting of hydrated basalt lithologies in amphibolite through garnet amphib- olite to eclogite facies has been viewed as particularly significant for the generation of the trondhjemitic-tonalitic components characteristic of Archean grey gneisses terrains (Martin, 1986). There is a strong possibility, for example, that partial melting of hydrated and subducted oceanic lithosphere was volumetrically more significant in the Archean than during the Phanerozoic.

There is an enormous literature devoted to the origins of granite (see Pitcher (1997) for a recent review), and a recent Clarke Memorial Lecture, with particular emphasis on the genesis of granitic suites in eastern Australia, has been published in this journal (Chappell, 1994). The issues being intricate and complex, debate continues (e.g. Chappell, 1998; Collins, 1998) on the relative importance of: i. fractional crystallisation from mafic precursors; ii. variable degrees of restite (unmelted but magma- tically equilibrated crustal source materials — see White and Chappell, 1977) separation; iii. magma mingling and mixing (of mafic and felsic end-members). A related topic of crucial importance is the nature of the heat source(s) sufficient to melt the crust thereby providing the energy sufficient to cause intra-crustal differentiation via granitic melt segregation from relatively refractory residues. Underplating of the crust by basaltic magmas has been invoked as a heat source (Raia and Spera, 1997), end-member of magma mixing (Collins, 1998), and a source of prominent deep crustal reflectors in some sections (e.g. Taylor and McLennan, 1995).

For the purposes of this paper however, the critical point is that the granitic upper continental crust is fundamentally generated, at least through the late Proterozoic and Phanerozoic, by intra-crustal processing of one-or-more parental lithologies. The two important questions then become: i). what are the parental lithologies and how are they made? ii). can we reconcile our observations of the overall chemical stratification of the continental crust with models of intra-crustal processing?

CONTINENTAL CRUST MANUFACTURE – THE PROTOLITHS

Concurrent with and subsequent to the development of the plate tectonic paradigm during the 1960s, a number of petrologists and geochemists (e.g. Coats, 1962; Taylor, 1967; Green and Ringwood, 1968; Ringwood, 1974) proposed a tectonomagmatic cycle that could generate the dioritic/andesitic composition that is still recognised as our best estimate of the bulk continental crust (i.e., with ~59 wt. SiO_2) (Table 1). In bare outline, this model proposes:

1. formation of basaltic oceanic crust at a divergent (i.e., mid-ocean ridge) plate boundary;
2. partial hydration of this crust through hydrothermal circulation of ocean water near the ridge crest, with further hydration during migration to a subduction zone;
3. subduction accompanied by heating of the oceanic crust to the point where partial melting occurs – the melt has the composition of andesite;
4. eruption, intra- and underplating of andesite in an island arc.

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5. peripheral welding of the arc to a continental nucleus;
6. intracrustal processing (i.e. partial melting) leading to the development of a buoyant, granitic, uppermost continental crust, and a more mafic, residual, and relatively dense lower crust.

This type of model is appealing in its simplicity and remains frequently cited in introductory Earth science texts (e.g. Skinner and Porter, 1995; Christopherson, 1997) whereas others (e.g. Chernicoff, 1995; Davidson *et al.*, 1997) have recognised the geochemical and geophysical difficulties that exist with this type of model. These difficulties are:

1. In intra-oceanic arcs remote from contamination by pre-existing continental crust, basalts are present among the eruptive rock types. Arculus (1981) suggested that the supra-Moho bulk compositions of these arcs are basaltic rather than andesitic. The geochemical

characteristics of basalt – andesite – dacite – rhyolite suites in these arcs are certainly consistent with the basalts being parental to the more SiO_2-rich compositions through fractional crystallisation (see Gill, 1981, for review). The variety of basalts in island arcs is large ranging from low-alkali, tholeiitic types through to highly alkaline (feldspathoid-bearing) and picritic magmas (e.g. Arculus, 1994).

2. The major source region of these basalts is the upper mantle, most probably the wedge of material overlying the subducted oceanic lithosphere (Pearce and Parkinson, 1993). Volumetrically minor but geochemically distinctive (in terms of volatile components and hydrophile trace elements) contributions derived from the subducted lithosphere can be recognised in terms of specific trace element fractionation patterns and isotopic characteristics of island arc basalts (e.g. Pearce and Peate, 1995).
3. Thermal modeling of present-day subduction zones (Peacock, 1990; Davies and Stevenson, 1992) shows that with the exception of young (and therefore relatively hot) oceanic lithosphere (<10 Ma), the subducted ocean crust is below its solidus at all depths below island arcs, and undergoes dehydration rather than direct partial melting.
4. There are only a restricted number of localities among the present global system of subduction zones where rocks of intermediate (i.e., andesitic) composition can be recognised as partial melts of subducted lithosphere. These are the distinctive adakites characterised by marked enrichments of the light compared with the heavy REE (Kay, 1978; Defant and Drummond, 1990). Other primary (in the sense of direct partial melting derivation from a protolith rather than by fractional crystallisation) intermediate rocks are boninites and associated rocks which clearly, however, result from hydrous partial melting of refractory peridotitic lithologies, most likely located in the shallower portions of the mantle wedge (see Crawford, 1989).

A significant problem arises, of course, if net continental compositional growth has been basaltic. Although intra-crustal partial melting of hydrous mafic lithologies is known to be capable of producing granodioritic compositions (e.g. Rapp and Watson, 1995), the volumetrically more abundant residue must be more mafic than basalt and be located somewhere in the continental lithospheric column. These extensive materials have not been identified in deep crustal granulite terrains or xenolith suites. Recognising this problem, a number of authors have invoked partial lithospheric delamination and recycling of the ultramafic residues from granodiorite production back into the mantle (e.g. Kay and Kay, 1991; 1993, Kay *et al.*, 1992), possibly to form the "enriched" mantle component labelled as EM1 (Hofmann, 1997). There is good evidence that delamination of the lowermost continental crust and sub-continental mantle lithosphere does occur in continent-continent collisions such as the Alps (Marchant and Stampfli, 1997). Note that a mafic lower crust of ~15km thickness, as currently estimated in recent reviews (Rudnick and Fountain, 1995), is volumetrically insufficient and compositionally too evolved to represent the complement of an intermediate to granodioritic middle and upper continental crust, if the original protolith was itself basaltic.

Even if a basaltic lower crust represents an underplated heat source driving intracrustal differentiation, we are still faced with the problem of sliding the filling out of the middle of the crustal sandwich. The filling in this case should be a volumetrically generous (ultramafic) residual complement of the felsic upper continental crust, with both overlying a deeper, lower crustal mafic layer.

It has been argued, most forcefully by Armstrong (1968; 1991), that the major episode of continental crustal growth occurred early in the Archean and that events subsequently have involved nothing more than recycling on a large (i.e., mantle – crust) scale with no net subsequent additions to the continental crust. In this extreme form, the problem of removal of ultramafic cumulates or residues is avoided, especially if the style of felsic melt generation in the Archean involved direct partial melting of hydrated and recycled mafic crust. There is ample isotopic evidence for extensive major intra-continental crust recycling (Vervoort *et al.*, 1999), but also unequivocal evidence for juvenile (contemporaneous derivation of a mafic component from the upper mantle) continental crustal additions (McCulloch and Wasserburg, 1988; McCulloch & Bennett, 1994) through the Proterozoic (e.g. Berrimian of west Africa — Boher *et al.*, 1992), Paleozoic (Lachlan Fold Belt — Gray *et al.*, 1997; Collins, 1998; and Altaids — Sengör and Natal'in, 1996), and Mesozoic (New England Fold Belt — Chappell, 1994).

Although many geochemists and petrologists regard convergent margins as the primary factory for continental crustal production, it is worth noting that a growing band advocate a prominent role for oceanic plateau accretion (e.g. Hill *et al.*, 1992; Abbott *et al.*, 1997; Albarède, 1998). Oceanic plateaus are generally believed to be the melting products of mantle plume heads, with volumetrically large basaltic piles formed in a restricted time frame (e.g. Coffin and Eldholm, 1994). Although supra-subduction zone magmas are the <u>only</u> basaltic type to share the prominent and distinctive continental crustal characteristic of low Nb/U and Ce/Pb (Hofmann *et al.*, 1986), it can be argued that this reflects a minor addition of arc magmas to a volumetrically more abundant oceanic plateau lithology.

Some features of oceanic plateaus are attractive from the point of view of involvement in continental crustal genesis:

1. Clear Phanerozoic examples exist for the accretion of extensive oceanic plateau terranes in western North America (i.e., Wrangellia, Howell, 1989) and Ecuador (Arculus *et al.*, 1999;
2. Basaltic crust is unsubductable when thicknesses exceed ~25 km (Abbott *et al.*, 1997) — in the case of the world's largest extant oceanic plateau (Ontong Java, east of Papua New Guinea, the Solomon Islands, and Vanuatu), the crustal thickness averages ~35km. Subduction of the Pacific Plate westwards along the Vitiaz Trench ceased with the docking of the entrained Ontong Java Plateau triggering partial obduction of the Plateau in the Solomons, and a subduction polarity reversal. A long-term addition to the continental Australian Plate of some Plateau material is probable. It seems likely that the Caribbean Plate, ringed by suprasubduction zone activity, is the thick basaltic crust formed by melting of the Galapagos plume head (Kerr *et al.*, 1997). Again, preservation of volumetrically significant oceanic plateau material as a basement to and in the core of arc magmatic products is possible ;
3. The episodic pattern of continental crust formation recognised in Arabia and west Africa (Boher *et al.*, 1992) seems to be more consistent with the style of mantle plume episodicity than

the supposed continuum of subduction zone activity (Albarède, 1998);

4. A significant plume component in continental crustal genesis provides a clear element transfer mechanism from the relatively fertile (in terms of incompatible elements such as Cs, Rb, and Th) deeper mantle. Continent construction via the tapping of a MORB-like mantle wedge in supra-subduction zone environments together with components from subducted MORB is challenged by the strongly depleted (in terms of incompatible trace elements) character of these upper mantle sources.

The overall role of oceanic plateaus in continental crust genesis is pursued further in a later section of this paper. Here it is worth noting that there is unequivocal agreement that the bulk composition (supra-Moho) of any oceanic plateau is predominantly basaltic. Accordingly, we again encounter the fundamental problem encountered with respect to arc protoliths of reprocessing a basaltic building block into a granodioritic upper crust without retaining the complementary ultramafic residue at depth.

CONTINENTAL CRUST MANUFACTURE – THE RESIDUES

On a global scale, it is clear that a mass balance, approaching non-volatile relative chondritic abundances, can be achieved in the primitive mantle between the incompatible element-enriched continental crust and the mantle source regions (now) of MORB (e.g. Allègre, 1997). In this sense, we understand in general terms where the residue of continental crust formation is located. On a more detailed scale however, it is not so obvious where the residues are situated of the second stage of processing that appears to be required in the sequence from:

$$\text{peridotite} \rightarrow^{\text{stage 1}} \text{basalt/high} - \text{Mg andesite} \rightarrow^{\text{stage 2}} \text{diorite } (\textit{sensu lato}).$$

The problem of disposal of mafic- ultramafic residues is in fact generic to all models of continental crust formation. The dynamics of subduction zone environments provide perhaps the simplest resolution to the general problem, particularly if intermediate-felsic melts can be separated from a mafic subducted lithosphere, and transferred to the surface, more-or-less unmodified compositionally. Continued subduction and recycling of the slab residues into the mantle is inferred. This type of model has been adopted by a number of authors to account for the typical granite–greenstone and tonalite–trondhjemite–granitoid (TTG) terrains of Archean continental crust, characteristic for example, of the Kapvaal (southern Africa), Dharwar-Karnataka (southern India, and the Pilbara and Yilgarn cratons of West Australia. Martin (1986) made the seminal suggestion that a secular change in subduction zone tectonomagmatism has occurred from Archean to Phanerozoic; partial melting and formation of TTG magmas directly from subducted garnet amphibolite-eclogite occurred in the Archean whereas dehydration of subducted lithosphere, triggering basalt-forming partial melting of the peridotitic overlying mantle wedge, has been the prime Phanerozoic mode of activity. Taylor and McLennan (1995) conclude:

> *... a somewhat different tectonic regime operated in the Archean and was responsible for the growth of much of the continental crust. Archean tonalites and trondhjemites may have resulted from slab melting and/or from melting of the Archean mantle wedge but at low pressures and high*

> *temperatures analogous to modern boninites.*

There is no requirement in models that invoke subduction zone environments for the formation of a dioritic continental crust, that the upper mantle underlying the crust need have any genetic relationship to the overlying crust. In modern intra-oceanic island arcs, the stability of geochemical compositions through ~50 m.y. of evolution is strongly indicative of continued mantle wedge replenishment by advective coupling with the downgoing subducted lithospheric slab (Arculus *et al.*, 1995). If the primary melt flux to an arc is basaltic, as argued by Arculus (1981), the problem remains of disposing of the residues from the basalt $\rightarrow^{\text{stage 2}}$ diorite of crustal formation, but the refractory residue from melting in the wedge plus the dehydrated subducted slab are advected and recycled into the mantle.

Another important observational constraint on models of continental crust genesis is the nature of the underlying lithospheric mantle (see Anderson (1995) for discussion of this term). It has been known for a long time that extraction of basalt from an upper mantle peridotite leaves behind a residue that is modally enriched in olivine and orthopyroxene, has higher $100^*\mathrm{Mg}/(\mathrm{Mg} + \mathrm{Fe}^{2+})$ (i.e., Mg#), and is depleted in Ca, Al, Ti, Na, and K. This residue is less dense than the original (pre-melting) peridotite. Of particular importance here is the negative correlation of forsterite content in olivine with density. The question can be posed: how does relatively buoyant, melt-depleted peridotite, ever become sufficiently dense to be recycled into the mantle? For the oceanic lithosphere, the answer lies with the increase in density consequent to conductive cooling of the oceanic lithosphere at the Earth's surface .

Observational facts concerning subcontinental peridotite xenoliths transported to the surface by kimberlites and alkali olivine basalts, are: i) that they have unusually high Mg#'s compared with other peridotite samples; ii) those that are derived from sub-Archean cratons are markedly enriched in orthopyroxene compared with calculated and experimentally-produced residues from mantle melting (Kelemen *et al.*, 1998); iii) in some cases, model ages (e.g, from Nd and especially Os isotopic systems) correspond to the major formation ages of overlying continental crust (e.g. Walker *et al.*, 1989).

Griffin *et al.* (1998) have documented a secular change in the nature of the sub-continental lithospheric mantle, noting: i) subcalcic harzburgites are present only in mantle beneath Archean terrains; ii) mildly subcalcic harzburgites are common beneath Archean terrains, less abundant beneath Proterozoic terrains, and essentially absent beneath NeoProterozoic and Phanerozoic terrains. Griffin *et al.* (1998) comment that the degree of depletion (in basaltic components) has gradually decreased in peridotite preserved in subcontinental lithospheric mantle, observing:

> *The Archean-Proterozoic boundary represents a major change in the processes that form continental lithospheric mantle; since 2.5 Ga there has been a pronounced, but more gradual, secular change in the nature of these processes. Actualistic models of lithospheric formation based on modern processes may be inadequate, even for Proterozoic time. The correlation between mantle type and crustal age indicates that the continental crust and underlying lithospheric mantle are formed together, and generally stay together for periods of eons.*

It is important to make some other points with respect to these observations. Firstly, the combination of high Mg#'s with high modal orthopyroxene in fact cannot be accounted for simply as representing residues from large percentages of partial melting, such as those that might have occurred in association with komatiite (ultramafic lava) development. Kelemen *et al.* (1998) have argued that a 2-stage process is in fact required: i) orthopyroxene-poor, high-Mg# shallow residues were formed as the result of high degrees of polybaric melting; ii) modal orthopyroxene was increased as a result of melt-peridotite reaction involving relatively SiO_2-rich melts (i.e., TTG) of subducted lithosphere. Secondly, even if some of the lithospheric mantle underlying continental crust is residual from crustal formation, it as an absolute requirement from the mass balance arguments presented earlier that a dramatically greater fraction of the residue <u>must</u> have been recycled into the mantle. The buoyant, high-seismic velocity lithospheric mantle roots beneath continents extend to ≥200 km (Jordan, 1988; B.L. Kennett, pers. comm. 1999); the portion of the mantle that has been affected by continental crustal extraction is at least ~60% and any residual root would have to extend nearly to the mantle-core boundary (allowing for the fact that continents occupy only 30% of the Earth's surface area). Thirdly, Handler *et al.* (1997) note that peridotite with Proterozoic Os model ages extends well to the east of current surface exposures in Australia, and may have no relationship with the overlying crust. Similarly, Richardson and Harris (1997) have commented on the disjunction between Os model ages for sub-continental lithosphere and major crustal-forming events.

My attempts to integrate some aspects of these models are presented in the discussion. I note here a problem with respect to the stratigraphy of the Archean continental lithosphere analogous to that of the "British ham sandwich" or "where is the filling?" Assuming that a high degree of polybaric partial melting (equivalent to ~30%), was involved in raising the Mg# of the residual lithospheric peridotite from a primitive value of ~90 to 93, then a pile (= 0.3 of the lithospheric root of ~150 km) approximating at least 50 km thickness of komatiites (and basalts) must have formed a crustal complement to this refractory residue. There is in fact no seismic evidence that thick mafic-ultramafic crust now exists beneath the TTG-dominated upper Archean continental crust, even granted the extent of surface outcrop of these kinds of basaltic lithologies. So we are forced to identify a process that would "slide out the mafic-ultramafic filling" from between the overlying SiO_2-rich crust and underlying refractory, lithospheric mantle. This does not constitute a simple delamination process.

MASS FLUXES AT CONVERGENT MARGINS

The mass fluxes at convergent margins include: the proportion of the down-going lithosphere that is accreted to the overriding plate; the materials that survive to be subducted into the mantle; the components that are released into the overlying mantle wedge over a range of pressures and temperatures down-dip, and those that survive to be recycled deeply within the Earth; and finally, the materials that are transported from the wedge to the overriding plate. Understanding the dimensions of these fluxes is important not only in the context of continental growth, but also the dynamics of the way the Earth works. For example, the atmospheric-hydrospheric-biospheric C cycle is moderated in the long term by fluxes into and out of the solid Earth, and the size of the C stocks ("reservoirs") within the Earth. We know that substantial amounts of marine carbonates are subducted, and assume a steady state is maintained by a return flux primarily through subduction zone volcanism. But at present, we have no firm data to support this assumption.

Subduction zone processes are complex and many aspects are contentious (e.g. Pearce and Peate, 1995). But there are several attractive features of the geochemical composition of supra-subduction zone magmas that render them popular candidates as key components of continental crustal genesis. The apparent equivalence of average andesite with a plausible bulk continental composition inspired Taylor (1967) to propose the "andesite model" of continent genesis. More recently, the striking fact that only supra-subduction zone magmas have been recognised to possess the low Nb/U and Ce/Pb (compared with MORB and OIB, see Hofmann *et al.* (1986)) characteristic of the continental crust has seemed to be a powerful argument that arc systems must be involved to some significant extent in the formation of continents. The critical point is that fractionation of Nb/U and Ce/Pb appears to require the involvement of fluid (i.e. plausibly supercritical hydrous) in addition to a silicate melt/residue fractionation event, and this is most likely to occur in the subduction zone rather than MORB or OIB environment (e.g. Arculus, 1994). And not the least of the considerations required of supra-subduction zone magmatic activity is the fact that clearly a flux of material is erupted at present-day convergent plate margins. These materials furthermore, do not obviously have the same short residence time at the Earth's surface that is experienced by oceanic lithosphere. In other words, the volcanic and plutonic rocks formed at island and continental arcs are not subducted *en masse* within ~10^2 m.y. Accordingly, it is sensible to consider what the magnitudes of mass fluxes at supra-subduction zones are, and what impact these might have on continental crustal growth. For example, in the extreme, we might discover that the volumes are so trivial as to be insignificant .

As a starting point, the linear growth rate required to produce all of the continental crustal volume in ~$4*10^9$ y (the age of the oldest crust) is ~1.6 km^3 a^{-1}. This really should be considered as an incremental linear survival rate because we have neglected erosion and subduction of continental materials. From this point onwards however, we encounter considerably greater difficulties in our mass flux calculations for convergent margins than is the case, for example, with computation of the rate of oceanic crust production. In this latter situation, we can straightforwardly take the average rate of ocean floor spreading (e.g. 5 cm a^{-1}), the total ridge length (~$5.5*10^4$ km), and the average crustal thickness (7 km) to calculate a present-day production rate of ~20 km^3 a^{-1}, equivalent to ~360 km^3 per km of ridge length per million years of spreading activity. By way of comparison, Reymer and Schubert (1984) estimate average production rates of oceanic crust production from the Mezozoic to Cenozoic of 25 km^3 a^{-1}, equivalent to 450 km^3 km^{-1} strike length m.y.$^{-1}$.

In the case of island and continental arcs, the situation is complicated by the facts that: 1. very poor constraints exist in general concerning the nature (proportion and age) of the basement of any arc; 2. the time interval over which any given volume of arc magmas has accumulated is generally not well known; 3. the nature and

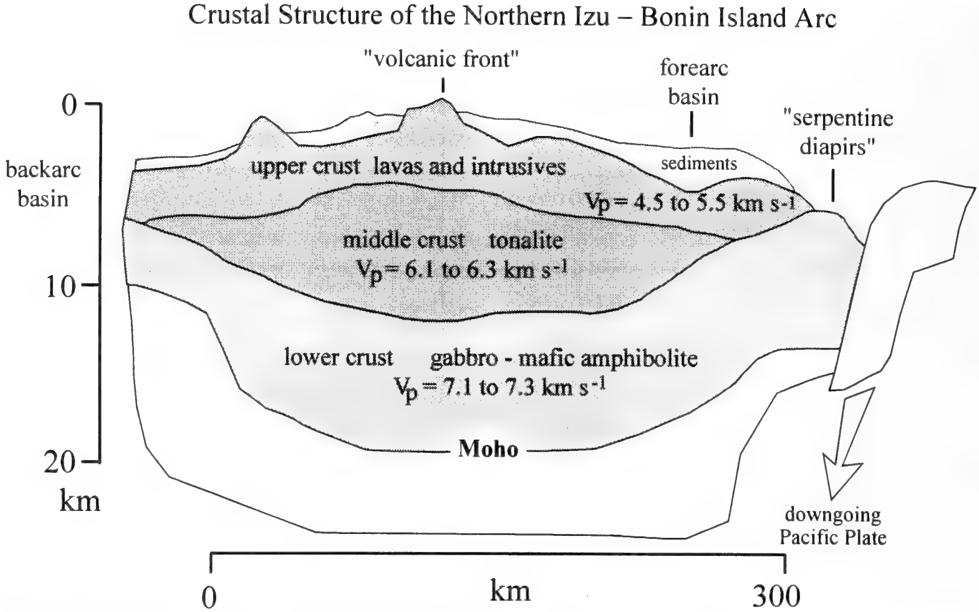

Fig. 2. The crustal structure of the Izu-Bonin island arc between the latitudes of 31 to 33°N, after Suyehiro *et al.* (1996).

depth of the Moho are typically poorly constrained. Accordingly, it is difficult to determine what the crustal production rate is at present-day convergent margins. Nevertheless, Reymer and Schubert (1984) presented the results of a valiant attempt to surmount these difficulties. For intra-oceanic arcs, they calculated arc volumes from seismically-derived crustal profiles, subtracted the equivalent of 6 km of "oceanic basement" upon which the arcs were assumed to have been built, and assumed durations of activity from estimates of dates of arc inception. The average arc crustal addition rate resulting from their estimates is 30 km^3 km^{-1} arc strike length $m.y.^{-1}$. Given the total present-day, active arc length (~3.7 * 10^4 km), a global production rate of 1.1 km^3 a^{-1} is derived. Despite the nature of the assumptions built into this estimate, it is important to realise that 1.1 km^3 a^{-1} is within the range (1.6 km^3 a^{-1}) required of a (conservative) linear growth rate for the continental crust. Conversely, if this arc flux is not to be important in continental crustal growth, then at least this volume of arc materials must be removed from the continents each year.

In the past few years, the results of a major controlled-source, two-ship seismic reflection-refraction survey of the intra-oceanic Izu–Bonin arc between latitudes of 31° to 33°N have become available (Suyehiro *et al.*, 1996; Takahashi *et al.*, 1998). Allied with our comprehensive understanding of the tectonic and magmatic evolution of this arc system, stemming primarily from decades of on-land and particularly deep sea drilling programs (e.g. Taylor, 1992), we have the opportunity for the first time of attempting a well-constrained, arc crustal growth calculation. The Izu–Bonin crustal profile is reproduced in Fig. 2. Specific aspects of the velocity profile will be addressed below, but the initial concern is to utilise:

1. the difference in thickness between the remnant arc (Palau – Kyushu Ridge ~10 km thick; Li *et al.*, 1997) and the active arc (20 km thick) at ~10 km;

2. during the opening of the Shikoku backarc basin and abandonment of the Palau–Kyushu remnant arc, there was minimal (if any – see Taylor, 1992; Arculus *et al.*, 1995) arc activity;
3. the incremental (10 km) thickness of the Izu–Bonin active arc was created in the 15 m.y. following cessation of backarc spreading and resumption of arc activity;
4. the width of the active arc is 300 km.

Then we calculate an arc crustal growth rate of ~200 km^3 km^{-1} arc strike length $m.y.^{-1}$ (Arculus, 1996). This is equivalent to a global arc production rate of 7.4 km^3 a^{-1}. Taira *et al.* (1998) made a similar calculation assuming the arc was constructed on 6 km-thick oceanic crust and was constructed over 45 m.y. (assumed age of inception, now known to be at least 49 Ma (Cosca *et al.*, 1998)) resulting in a flux of 80 km^3 km^{-1} arc strike length $m.y.^{-1}$ or global production rate of ~3 km^3 a^{-1}. If the protoarc was formed in an extensional (but still supra-subduction zone) environment, and not built on any pre-existing oceanic basement, as argued by Taylor (1992), then the crustal growth rate to produce the entire 300 km wide * 20 km thick arc crust in ~50 m.y. is 120 km^3 km^{-1} arc strike length $m.y.^{-1}$. The main point to note about these figures is they are a factor of 3 to 6 times greater than the global average estimate of Reymer and Schubert (1984).

There are of course, a number of difficulties and problems with these specific estimates as well as dangers inherent in extrapolation of the figures:

1. the estimates are for a comparatively limited period of time for an intra-oceanic arc with episodic growth, that has undergone strong rotation since inception (Hall *et al.*, 1995; see also: http://www.gl.rhbnc.ac.uk/seasia/html/globalview.html;
2. we assume magmatism (intra- and underplated) has occurred over the full arc width of 300 km; in general, however, the major eruptive flux of magmas in arcs appears to be limited to the "volcanic front" – the specific locus marking the nearest-to-trench volcanic activity. Nevertheless, we know from intersection through drilling in the Mariana forearc of a Pleistocene sill (Marlow *et al.*, 1992) that the extent of forearc construction through magmatism has likely been underestimated.

There are a number of other interesting comparisons that stem from these types of magmatic flux calculations, and the specifics of the Izu–Bonin crustal structure. For example, the flux of H_2O into-and-out of subduction zones is particularly interesting from the point of view of overall steady state of the hydrosphere. If we assume that the full 7 km of altered and subducted Pacific oceanic crust contains 2 wt. H_2O (e.g. Peacock, 1990) and is subducted at a rate of 100 km $m.y.^{-1}$, then given a rock density of 2800 kg m^{-3}, the rock mass flux into the subduction zone is ~$2*10^{15}$ kg km^{-1} strike length $m.y.^{-1}$, and the subducted H_2O flux is ~4 * 10^{13} kg km^{-1} strike length $m.y.^{-1}$. How does this compare with the flux of H_2O out of the Izu–Bonin island arc volcanoes? Estimates of the amount of dissolved H_2O in basaltic arc magmas are generally in the range of 2 wt. H_2O (e.g. Pearce and Parkinson, 1994). For steady state, therefore, and if the only return path to the Earth's surface for H_2O is via arc volcanism, then a return mass flux equivalent to the input is required of 700 km^3 km^{-1} arc strike length $m.y.^{-1}$ and a H_2O flux of 4 * 10^{13} kg km^{-1} arc strike length $m.y.^{-1}$. With the Reymer and Schubert (1984) arc crustal growth estimate, and assuming 2 wt. H_2O is dissolved in parental arc basalts, the H_2O flux out of arc systems is ~20 times less than the amount subducted. With the larger arc crustal growth values presented by Arculus (1996) and Taira *et al.* (1998), the discrepancy between H_2O fluxes is reduced by up to a factor of 3.5.

Not all of the subducted H_2O flux of course may be emitted via arc magmatism. We know for example, that a significant quantity (but precise flux unknown) of subducted slab-derived fluids are emitted in the forearcs of the Izu–Bonin – Mariana systems from serpentine-hosted vents (Fryer *et al.*, 1995). In addition, on the basis of trace element and isotopic systematics, it is known that backarc basin magmas also contain subducted slab-derived H_2O (see Stolper and Newman, 1994). In the case of the Mariana system, if we take the full width (~1200 km) of the two backarc basins (Parece Vela and Mariana Trough), assume a crustal thickness of 7 km and a combined duration of backarc spreading of ~30 m.y., then a backarc oceanic crust production flux of 400 km^3 km^{-1} ridge strike length $m.y.^{-1}$ is calculated. With a maximum of 1 wt. H_2O dissolved in these backarc basin basalts, a combination of concurrent arc and backarc basin magmatic activity (assuming an arc crustal growth rate of ~100 km^3 km^{-1} arc strike length $m.y.^{-1}$) can account for ~$^1/_2$ of the subducted Pacific Plate H_2O input flux. Finally, a variety of potential mineral hosts exist for H_2O in the subducted slab (e.g. Schmidt and Poli, 1998) that might bypass all of the forearc, arc, and backarc extractive processes, and be recycled deep into the mantle. It is clear therefore, that better estimates of the crustal growth rates in arcs are crucial for a variety of elemental budget calculations. The low values of Reymer and Schubert (1984) require greater H_2O fluxes in one or more of the processes controlling forearc, backarc, or deeply recycled subducted slab processes.

There are other aspects of the Izu–Bonin seismically-determined crustal profile (Fig. 2) that merit further consideration. The most striking of these is the presence of a layer between 5 and 15 km depth with a V_p of 6.1-6.3 km s^{-1}, consistent with a granitic (*sensu lato*) composition (Suyehiro *et al.*, 1996; Takahashi *et al.*, 1998). Taira *et al.* (1998) suggest that this layer corresponds to the tonalitic (~66 wt. SiO_2) plutons (Kawate and Arima, 1998) outcropping in the Tanzawa Mountains of the accreted (to Honshu) Izu–Bonin arc crust. Depending on the assumptions made concerning the compositions of the other layers, Taira *et al.* (1998) estimate a bulk overall andesitic (54 wt % SiO_2) composition for the Izu–Bonin arc crust, and question whether the assumption by Arculus (1981) of a bulk basaltic composition for intra-oceanic arcs is correct.

There are however, a number of alternative conclusions that can be drawn from the evidence concerning the structure of the Izu–Bonin crust. In my view (e.g. Arculus, 1994), there is unequivocal evidence both from the widespread examples of basaltic magmas erupted in arcs together with extensive experimental evidence, that basalt is the primary (wet) partial melting product of the peridotitic mantle wedge. There is also considerable observational and theoretical evidence for the prevalence of fractional crystallisation processes in arc systems (e.g. Gill, 1981). The crystalline phases that dominate the earliest cumulates in basaltic arc magmas are spinel-olivine-clinopyroxene, given the suppression of plagioclase crystallisation by dissolved H_2O. Accepting the fact that the bulk composition of the supra-Moho Izu–Bonin crust is a mafic andesite, I suggest that the bulk of the early-formed olivine–clinopyroxene-rich cumulate phases are in fact located below the Moho. Furthermore, in the longer term, it is likely that these materials are incorporated in the advecting mantle wedge (H. Davies, pers. comm., 1999), or in other words, swept away from the base of the arc crust and recycled into the mantle.

It is an interesting fact that exposed examples of olivine – clinopyroxene-dominated plutonic roots of island arcs are rare (cf. Pearcy *et al.*, 1990). We might expect that deep crustal sections of island and continental arcs would more commonly expose the type of dunite–clinopyroxenite–websterite cumulate sequences characteristic of the Jijal Complex of Kohistan (Jan and Windley, 1981). In the case of this deeply exhumed Himalayan example however, garnet is an important phase of the more evolved mafic cumulate pile that was developed at the base of a Mesozoic arc. There is no support in general for the fractional crystallisation of garnet in the intra-oceanic arc sequences of the Izu–Bonin system. A much closer analogue in terms of predicted phase sequence and calculated melt compositions to the early fractional crystallisation products of the tholeiitic arc basalts of the Izu–Bonin system, is the layered Permo-Triassic Greenhills Complex of the South Island of New Zealand (Mossman, 1970; Spandler, 1997) where dunite, olivine clinopyroxenite, and gabbro form the most mafic layers. Cumulate blocks of appropriate phase proportions and composition are among the volcanic ejecta of a number of arcs (e.g. Arculus and Wills, 1980; Conrad and Kay, 1984). But the point remains that volumetrically extensive, ultramafic-mafic sub-arc cumulates are not prominent components of the continental crust. It appears that advective sweeping into the mantle wedge of these materials generally, and recycling into the mantle is a plausible model that fits all of our present observational and theoretical facts.

A corollary of the suggestion that a cumulate fraction of the basaltic flux from the mantle wedge may be located sub-Moho for the Izu–Bonin system, is that the total supra-subduction zone flux in this instance is greater than the estimates of 80 to 200 km^3 km^{-1} arc strike length m.y.$^{-1}$ based on supra-Moho volumes alone. This has several consequences, not the least that the arc H_2O flux is larger than that calculated from crustal volumes and H_2O concentrations in basalt alone. The imbalance between subducted input and total output thereby is reduced.

A linear survival rate for growth of the continental crust requires a net addition of ~1.6 km^3 a^{-1} whereas the apparently conservative, present-day estimate by Reymer and Schubert (1984) of arc crustal growth supplies only 1.1 km^3 a^{-1}. The volumetric deficit, if present-day convergent margins are representative of longer-term continental growth, is exacerbated by the fact that our best estimate (von Huene and Scholl, 1991) for the amount of continent-derived sediment that is subducted into the mantle is ~1 km^3 a^{-1}. The net deficit of ~1.5 km^3 a^{-1} of crustal growth can of course be readily supplied if the higher estimates of 3 to 7.4 km^3 a^{-1} fluxes estimated for the Izu–Bonin system are generalisable. Additionally, if the material supra-Moho fluxes are mafic andesite rather than basalt, then the required continental growth rate (= linear survival + subducted continent-derived sediment) can be satisfactorily balanced. Conversely, these present-day fluxes are embarrassingly large if island arcs are not involved in continental growth because the volumes significantly exceed that of the subducted sediment flux.

It is also of interest to compare estimates of the wedge-derived supra-subduction zone magma flux with calculations of the

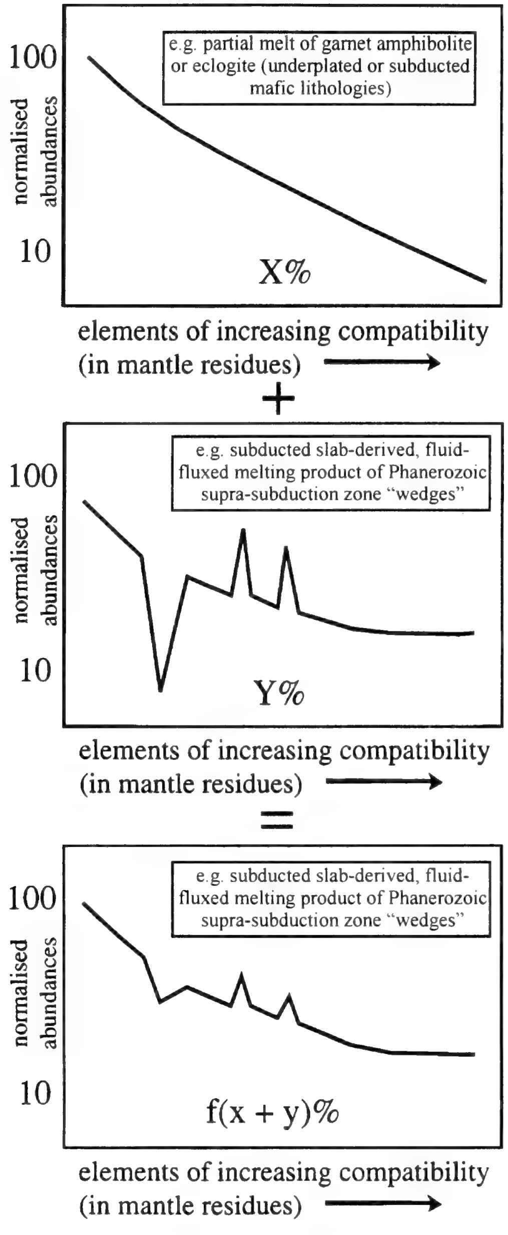

Fig. 3. Schematic representation of the effects of mixing, in arbitrary proportions (x, y) of different crustal types where x might be equivalent to Archean TTG compositions and y equivalent to Phanerozoic island arc basalt or andesite.

percentages of mantle melting involved. The strongly supported consensus view of MORB genesis is that the melts represent aggregates of fractional decompression melting of the mantle, equivalent to a total of 10 to 15% melting (e.g. Langmuir *et al.*, 1992). Exploring the systematics of non-hydrous fluid-mobile trace elements in supra-subduction zone magmas, Pearce and Peate (1995) calculate total melting percentages for intra-oceanic arcs (e.g. Marianas, Vanuatu, Tonga-Kermadec) of 15 to 30%. A combination of greater % of partial melting in combination with lower total magma flux in the arc compared with the mid-ocean ridge case must reflect either the involvement of a smaller volume of mantle in the supra-subduction situation, or episodic magma generation. The recent suggestion by Eggins and Rudnick (1999) that arc magma generation involves a disequilibrium process (essentially "flash" melting) along channelised paths is consistent with large %'s of partial melting of restricted mantle volumes.

GENERAL DISCUSSION

If inferences concerning the recycling into the mantle of the mafic complement of intermediate to felsic components of the intra-oceanic Izu–Bonin arc are globally valid, then the major objection encountered with respect to Late Proterozoic to Phanerozoic basaltic arc magmatism as a major contributor to continental crustal growth is negated. It would appear overall, that the original "andesite" model of Taylor (1967) offers the best general solution to the problem of the origin(s) of the continental crust. However, a number of other problems and qualifications necessarily arise.

There is strong observational evidence for a significant change in the nature of continent-building protoliths during the Archean to Proterozoic transition (Taylor and McLennan, 1985). In summary, the Archean upper continental crust includes, as an abundant component, Na-rich TTG with relatively enriched light *versus* heavy REE abundances, an absence of a negative Eu anomaly, and with relatively short crustal residence times on the basis of coincidence of Nd model and absolute ages. In contrast, the later Proterozoic is characterised by K-rich granitoids with less light *vs.* heavy REE fractionation, the development of a significant negative Eu anomaly, and a growing discrepancy between the Nd model and absolute ages. This geochemical evidence is strongly supportive of a secular change from the partial melting of a garnet-bearing, plagioclase-free (either amphibolite or eclogite facies) mafic protolith in the Archean to the involvement of a major component of intra-crustal reprocessing and granitoid genesis involving residual feldspar in the Proterozoic. It can be inferred that this transition in crustal genesis style was also accompanied by a change from direct partial melting of subducted mafic lithosphere to dehydration followed by hydrous partial melting of the peridotitic mantle wedge (Martin, 1986). Note that the extensive recycling (i.e., mixing) of older with juvenile components does not obliterate the distinctive trace element fractionation patterns generated during these varied crustal formation processes (see Fig. 3).

Recycling into the mantle of the ultramafic-mafic complement to the juvenile mafic andesite component of continental crustal genesis from the Proterozoic onwards produces predictable geochemical signatures that may be recognised in subsequent melting products of the mantle. For example, on the basis of known trace element distribution coefficients, arc basalt-related cumulates (dunites, olivine clinopyroxenites, and gabbros) could potentially be characterised by:

1. low bulk Rb/Sr and time-integrated low $^{87}Sr/^{86}Sr$;
2. supra-chondritic Nd/Sm and hence time-integrated sub-chondritic $^{143}Nd/^{44}Nd$ (i.e. -veε_{Nd});
3. low Nb/U and Ce/Pb reflecting the marked enrichments of U and Pb in arc basalts relative to primitive mantle.

A major issue concerns the nature of the genetic link between the continental crust and underlying mantle component of the lithosphere. On the one hand, it can be argued from the evidence of prolonged lithospheric residence time, coincidence of Os isotopic model ages of mantle and overlying crust, plus the intrinsic buoyancy of high Mg# harzburgite, that a strong genetic link exists (e.g. Walker *et al.*, 1989; Griffin *et al.*, 1998). Countering this possibility is the geochemical requirement for removal of the great bulk of the ultramafic-mafic residues of dioritic crust formation, the fact that continental crustal deformation (either folding, thrusting, or extension) leads to substantial dislocation of crust and mantle (Clowes *et al.*, 1999), and the possibility that buoyant crust eventually is most readily preserved (but coincidentally) overlying buoyant mantle. A comment, for example, from the "Lithoprobe" transect of the southern Canadian cordillera is: '*A key observation is that rock units mapped on the surface are decoupled from the mantle and, in some cases, the crust upon which they formed, and are attached as thin flakes, or sheets, to the craton.*' (Clowes *et al.*, 1999). This latter situation can be termed the "lifeboat" model for continental crust preservation. For example, the highly depleted (more than beneath mid-ocean ridges) and buoyant mantle sections of oceanic plateaus represent the type of mantle which may end up in thrust contact and long-lived survival with overlying continental crust.

Intra-crustal differentiation with development of an uppermost granodioritic composition is likely driven by under- plating of basalt (e.g. Clemens and Vielzeuf, 1987; Raia and Spera, 1997). This kind of material therefore is not necessarily representative of the original (andesitic) protolith of continental crust, but most likely does become involved through mixing with the original crustal components. The basalt might include any of arc, hot-spot, or rift-related types. An active example of present underplating by hot-spot mafic magma with major intra-crustal melting is the Yellowstone system.

CONCLUSIONS

To a first approximation, the marked enrichment of a number of alkali elements (~100 fold) in the continental crust compared with estimates of primitive mantle abundances is matched by complementary depletions in the global mantle source regions tapped by mid-ocean ridge basalts. In other words, the "depleted mantle" source of the most abundant crustal rock type (oceanic) represents a residue from continental crust extraction. In fact, depending on the primitive mantle abundances chosen, it is probable that ~60% at least of the mantle has been involved in formation of the continental crust. Consequently, there is a strong geochemical argument that any depleted ("refractory") mantle component of the continental lithosphere can only represent a small fraction of the total mantle involved in continental crust formation. There can be no enduring retention of all associated residual mantle in any vertical, continental crust-mantle differentiation process, and any juxtaposition may simply represent a fortuitous linkage of buoyant crust and mantle.

We know that the dioritic-to-tonalitic major element composition of the continental crust can be produced in a variety of ways: (1) fractional crystallisation of basalt; (2) direct melting of subducted/ underplated mafic lithosphere; (3) fractionation of high-Mg andesites generated by melting of peridotite. All three of these processes require the presence of H_2O — hence the aphorism of Campbell and Taylor (1985): '*No H_2O no granite, no oceans no continents*'. And in detail, it is clear that much of the crust, while produced initially in the Archean and early Proterozoic, has been subjected to considerable intra-crustal recycling.

Trace element and isotopic systematics require (at some stage) in continental crust genesis: (1) low % of partial melting either in the mantle and/or within the crust; (2) garnet-bearing protolith involvement; (3) fluid/solid elemental fractionation to account for the marked enrichment of Pb compared with other trace elements of similar melt/solid incompatibility.

Temporal changes in continental crust genesis through Earth history have been important. Unquestionable continental crustal growth has taken place in the Phanerozoic (e.g. much of eastern Australia east of the Rodinia break-up margin; the Altaiids of central Asia (Sengör and Natal'in, 1996). Post-Proterozoic constraints stressing the significance of the involvement of H_2O are: **1.** without deep recycling of H_2O, neither melting of a subducted slab nor overlying mantle wedge occurs. Furthermore, the order of crystalline phase appearance in cooling basalt magmas containing a few % H_2O is: olivine, pyroxene, plagioclase — the delay in plagioclase appearance in the "wet basalt case" enhances concentration of Si, Al, Na, and K in residual magmas (key elements present in abundance in granites). The presence of hydrated minerals (amphibole/biotite) in crystallisation products of wet magmas is also important in generation of granitic magmas during ultra-metamorphism of continental crust. **2.** a key requirement for fractional crystallisation is for the system to "be left alone" (i.e., allowed to cool and crystallise) with minimal accompanying magma chamber tapping or replenishment. Neglect is a function of local magma flux, and in arcs, this is ~0.1 to 0.3 of the ridge flux. **3.** disposal of ultramafic/mafic crystalline cumulates from basalt fractionation processes is crucial for production of granodioritic crust. Cumulates may be partly underplated (sub-Moho) as part of the continental lithosphere or more likely, dynamically removed. Melts escaping from a supra-subduction zone system are not coupled to crystal cumulates and residual mantle; the latter are advectively dragged by the subducted lithosphere and recycled deep into the mantle. A summary of this Phanerozoic style of growth would emphasise "damp, neglect, and waste disposal" as crucial factors.

It is likely that a combination of several potential protoliths is required including: (1) wet partial melts of high-grade (eclogite, garnet amphibolite) mafic lithologies; (2) wet partial melts of the mantle involving recycled, subducted slab-derived H_2O; (3) some minor input of intraplate (plume-derived) magmas.

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BIOGRAPHICAL MEMOIR

SIR ROBERT PRICE

1912-1999

The death of Sir Robert Price earlier this year saw the loss of one of Australia's most prominent scientists whose active scientific career was crowned by chairmanship of the CSIRO. He was elected to Honorary Membership of the Royal Society of New South Wales in 1976.

Sir Robert Price was known widely to his friends and colleagues as Jerry, a nickname he acquired at school at St. Peter's College, Adelaide. After graduating (BSc, MSc) from The University of Adelaide, he was awarded an 1851 Exhibition to Oxford University, where his research under Sir Robert Robinson culminated in a D Phil. At the outbreak of war in 1939 Jerry decided to stay in Britain, where he was directed to work as a chemical inspector of munitions factories in Scotland.

In 1945 Jerry Price returned to Australia to commence research in the CSIRO on Australian native flora. This developed into a major program, the Australian Phytochemical Survey. Much research was carried out on the pharmacological and anticancer properties of several thousand species. In 1960, Jerry was made Officer-in-Charge of the Organic Chemistry Section which soon became a Division with him as Chief. He reorganised the research programs and initiated new projects in synthetic chemistry and natural products which led to interesting and innovative work, culminating in many good papers.

In 1966 Jerry Price joined the CSIRO Executive and from 1970 to 1977 he was Chairman. He is remembered for his firm, courageous stand against the Whitlam Government's attempt to remove research on minerals and solar energy from CSIRO to the Public Service. Most of us saw this as the first step in the break up of CSIRO. This move was defeated and CSIRO remains as a multidisciplinary research organisation. Jerry is surely admired for his strong defence of CSIRO which caused him some stress, hopefully eased, at least in part, by the wholehearted support of his colleagues in Canberra and of the staff nationwide. It must have been a unique experience to have the support of everyone in CSIRO!

Amongst the many recognitions of Jerry's career are a DSc (Adelaide) the Federal Presidency of the RACI, the H.G. Smith Medal and the Leighton Medal of the RACI and the Fellowship of the RACI and of the Australian Academy of Science. It was fitting that he was made a KBE a year before his retirement.

In 1940 Jerry married Joyce Brooke whom he had met at The University of Adelaide where she was studying science. She has a long and distinguished record with the Girl Guides Association of Australia and she also shared with Jerry a passion for the cultivation of native plants.

Although Jerry Price had a busy career he did not forget his friends and colleagues, especially young scientists. His engaging smile will be remembered with affection by those privileged to have known him.

Vale Jerry Price, respected scientist, valued friend and loving family man.

D.J.S.

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Thesis Abstract: Air Movement in the Human Sleeping Environment and Sudden Infant Death

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Abstract of a Thesis submitted for the Degree of Doctor of Philosophy
Murdoch University, W.A. 1999

Searches for disease or abnormality within the infant have not led to an explanation for many Sudden Infant Death Syndrome or SIDS cases. The present study considers SIDS in terms of the microclimate at the face and the inhalation of previously exhaled air. Inhalation of previously exhaled air is also known as re-breathing. The physiology of sleeping in re-breathing conditions and SIDS is discussed. Statistical data concerning SIDS and environmental conditions is reviewed.

The transport of carbon dioxide from and oxygen to the face is effected by jet action of the nose and other processes. Temperature, humidity, pollution (which affects aerosol formation), bedding arrangement, sleeping position and other conditions are significant. A simulator for studying sleeping environments is described. It was found that exhaled air can accumulate at the face of a sleeping infant. In some circumstances the carbon dioxide content of the inhaled air is above the industrial threshold limit of 0.5% with values of over 2% occurring.

Physiological mechanisms exist which allow that re-breathing of vitiated air can account for a proportion of SIDS cases. In particular a sleeping infant acclimatized to an atmosphere with excess carbon dioxide may suffer from a reduced lung ventilation rate [in medical terms a reduced minute volume] on subsequent exposure to a normal atmosphere.

The associations between SIDS and particular environmental conditions were found to be consistent with re-breathing as a cause of SIDS. It is recommended that sleeping infants have unobstructed passage of exhaled air away from the face. Detailed safety precautions are given. It is clear that investigations of SIDS deaths should include physical model studies of the infant's sleeping environment; follow-up SIDS investigations should include searches for evidence of past exposure to continual re-breathing.

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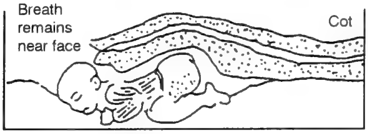
Sudden Infant Death, Crib Death (U. S. A. term for cot death), Cot Death and Overlaying (where baby dies in bed with mother) and now all described as SIDS, have been found to be more common in these circumstances: winter, low temperatures, high humidity, atmospheric pollution.

Explanation for a proportion of these deaths can be made in terms of the accumulation of exhaled air with excess carbon dioxide at the face during sleep. The result of continued sleeping in this environment is that the infant becomes acclimatized to a high carbon dioxide level in inspired air and the control of breathing becomes abnormal. Exhaled air from other persons or animals sleeping close to the face of the infant may also contribute.

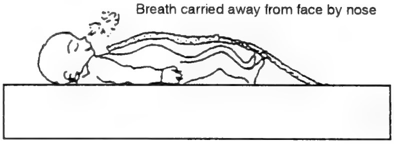
POSSIBLE DANGER



Conditions that make the retention of exhaled air in the bed more likely:-

*Soft bedding
*Bulky bedding near the face
*No draughts
*Face down position
*Damp or wet bedding
*Confined cot, pram or bed
*Unventilated mattress
*Infant under bedding
*High humidity (see note A)
*Tobacco smoke, air pollution
* Exhaled air directed into bed

SAFE



Conditions that make retention of exhaled air near the face less likely:-

*Hard bed
*Thin bedding
*Dry bed
*Face up position
*Draughts
*No bottles, toys or obstructions
*Not sleeping through the night
*Not exposed to breath of others (note B)
*Not sleeping between adults
*Not to sleep against a wall
*Mattress bedding not permeable
*Breath to direct air away from the face.

Note A: High humidity can result from climatic influences, unflued gas or kerosene heaters and evaporative air conditioners.

Note B: If in bed with adults the infant must not be down in the bed and exposed to a pool of exhaled air from the adults.

Always make sure that there is a clear space around the head so that the baby has access to fresh air. The breath coming from the mouth or nose is not obstructed so that it can move freely away from the face. Making sure that the baby gets fresh air will provide protection against the dangers of exhaled air at the face even if other conditions are bad.

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Thesis Abstract: Prediction of the Dimensional Accuracy of Small Extra-coronal Titanium Castings

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Abstract of a Thesis Submitted for the Degree of Master of Science in Dentistry
at The University of Sydney

The present study aimed at establishing a formula that predicts the dimensional accuracy of small extra-coronal titanium castings. The experimental component of the research started with determination of the metal shrinkage to be compensated. This was followed by the prediction of dimensional accuracy firstly using mould expansion data from manufacturers and then those from laboratory measurements. Three investments available for titanium casting were used.

The dimensional accuracy of dental castings has long been assessed using specially designed metal dies. Although full crown designs are very common for this purpose, the demand for porcelain veneered restorations is increasing and a new die design for this type was also introduced in the present study.

Finally, a statistical model was developed to examine the contribution of setting and thermal expansion to the accuracy of castings. It was hoped that the statistical approach would provide an answer to the hypothesis that the contribution of setting expansion of investment is little in the fabrication of small extra-coronal castings.

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Thesis Abstract: A Study of Some Ternary Tetradentate Complexes As Phenanthrene-based Chiral Metallointercalators

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Abstract of a Thesis submitted for the Degree of Master of Science,
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The main aim of this research was to investigate the synthetic and structural chemistry of the ternary Ru(II)-*picchxn-phdi* chelate system and to characterise the interaction of these chelates with DNA. The complex cations synthesised and characterised were *rac*-β-[Ru(picchxn)(phdi)]$^{2+}$, Δ-β-[Ru(*S,S*-picchxn)(phdi)]$^{2+}$, Λ-β-[Ru(*R,R*-picchxnmi)(phdi)]$^{2+}$, *rac*-β-[Ru(picchxnmi)(phdi)]$^{2+}$,Λ-β$_2$-[Ru(*R,R*-picchxnmi)(dmso)Cl]$^+$.Here *picchxn* represents *N,N'*-di(2-picolyl)-*1R*,2R**-diaminocyclohexane, *picchxnmi* refers to the monoimine form of the same, *phda* is 9,10-diaminophenanthrene, and *phdi* refers to the diimine form of the same. The compounds were obtained as their Cl$^-$ or PF$_6^-$ salts. The interaction of each of the *phdi* complexes isolated with calf thymus DNA was studied spectroscopically by visible absorbance hypochromism and circular dichroism (CD) titration methods. The absorbance titrations show DNA to be saturated at *ca* 3.6 base pairs per ruthenium complex for *rac*-β-[Ru(picchxn)(phdi)]$^{2+}$ and Δ-β-[Ru (*S,S*-picchxn)(phdi)]$^{2+}$, at *ca* 3.7 for *rac*-β- [Ru(picchxnmi)(phdi)]$^{2+}$, and *ca* 3.9 for Λ-β- [Ru(*R,R*-picchxnmi)(phdi)]$^{2+}$. The calculated intrinsic equilibrium binding constants range from 5.6 - 13 x 10^4 p, and the red shifts with accompanying hypochromism observed indicate that the complexes intercalate. The plotted extrema in CD titrations reveal the existence of two inflection points suggesting that more than one mode of binding exists in these systems. Titrations performed on racemic complexes suggest a Δ enantioselectivity. The red shift and positive induced CD (ICD) provide further evidence as to the mode of binding being intercalation. Equilibrium dialysis and ethanol co-precipitation experiments for the racemic complexes in the presence of calf thymus DNA also reveal a small degree of enantiomeric selectivity for the Δ enantiomer, with the optical enrichment values ranging between 4-18%. Thermal denaturation studies on free DNA and DNA-complex adducts show significant increases in T$_m$ upon binding of the cations, confirming that intercalation is the predominant binding mode. There is also an indication that the DNA interaction of these complexes is base sequence selective. Molecular modelling reveals that the one amine proton of *picchxn* is well positioned for H-bonding with O6 of a guanine residue when the complex is intercalated into a G-C site, which may be the cause of this selectivity.

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Thesis Abstract: Effect of Exercise on Diffusing Capacity in Patients with Cystic Fibrosis

RHONDA ORR

Abstract of a Thesis Submitted for the Degree of Master of Exercise and Sport Sciences at The University of Sydney 1995

Regular exercise has been increasingly emphasised as an important component in the management of the patient with cystic fibrosis. However, exercise imposes great stress on the pulmonary system and patients with cystic fibrosis can vary markedly in their exercise response. Patients with spirometry in the normal range exhibit a normal response to exercise. Patients with severe lung disease experience exercise intolerance, with hypoxaemia, hypercapnia and increased end-expiratory lung volume.

One aspect of pulmonary investigation is diffusion of gases during exercise. Diffusing capacity of the lung for carbon monoxide (D_{LCO}) increases with exercise in the normal population, but has not been demonstrated in patients with cystic fibrosis. The limited number of studies in this area give conflicting results, both at rest and after completion of exercise. Reports suggested that there may be a diffusing defect or diffusion limitation during exercise in patients with cystic fibrosis. To the author's knowledge, no studies have directly measured D_{LCO} during exercise in patients with cystic fibrosis, who have not undergone heart-lung transplantation.

The aim of this study was to measure D_{LCO} directly during exercise and to determine if there was a normal increase with exercise. Single-breath D_{LCO} was measured in twelve patients with cystic fibrosis and six normal subjects, at rest and during incremental steady state exercise to exhaustion, with five minute rest intervals between workloads. During exercise, all patients with cystic fibrosis significantly increased their single-breath D_{LCO} from rest, suggesting an ability to recruit alveoli and pulmonary capillaries by expanding the pulmonary capillary bed effected through an increase in cardiac output. Moreover, the rise in the diffusion rate was similar to that of normal subjects. There was no evidence for diffusion limitation during submaximal exercise in patients with cystic fibrosis.

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"Earth Universe Cosmos: an Inquest into Our Creeds" by S. Warren Carey, AO

Reviewed by JOHN C. GROVER, OBE

Published by the University of Tasmania in 1996, on the occasion of the 50th Anniversary of the Department of Geology, this book crowns the 60 year saga of Professor Carey's career, in support of arguments which question many teachings in the Earth Sciences. Professor Carey gives credit to modern and ancient ideas up until the 1990s. He notes that the Copernican model was proposed by Aristarchus two millennia ago and by Sanscrit Scholars 3000 years before him. Covering a wide field, subdivided into 11 chapters, each with major subdivisions, the book deals with the Earth, the Solar System and beyond. The work is supported by a good detailed Index and many references. One appendix deals with properties of the Members of the Solar System in a well-laid out numerical table. The other appendix deals with Dimensions of the Velocity of Light.

Beginning with **Fundamentals Of Existing Beliefs**, Professor Carey faces up to relevant issues:

> Man's vision of Nature is a mosaic of memes. Whereas a gene is a self-replicating organic unit, a meme is a self-replicating mental concept. Richard Dawkins coined the term meme, which starts from observed fact and is extended by intuition or faith to embrace apparent greater truths as a creed.
>
> ...The fact that the concept of God is a meme does not itself indicate truth or falsity. A meme may be absolutely true or quite false; but it is born from intuitive faith, not logical reason. Science began with memes, to explain the obvious but unexplainable behaviour of the heavenly bodies and occasional terrifying interlopers and the ever-present mysteries of life and death. (p. 1)

Carey points out forthrightly that the mosaics of memes which permeate and dominate the periodic "fashions" of the earth sciences, cannot be ignored because of the errors they introduce into the teaching of modern geology.

> ... The exercise I have attempted is to survey our classic dogma of geology, which is part of the wider fabric of astronomy, to ask whether some of the things we are taught as facts, indeed which I have taught, are really valid. (p. 7)

A powerful objective indeed from one of the few strong characters who took a stand for a quarter of a century on the essential value of Wegener's concept of 'continental drift', though virtually 'excommunicated' by the British scientific establishment.

The Principle of Uniformitarianism—that the present is the key to the past—was a dominant meme a century ago, but the ideas went back to Xenophanes (604-540 BC). Carey mentions:

> ...the Tollmans (1993, 1994) have argued that the Noah Flood was a real event some 10,000 years ago, recorded in the strewn fields of tectites and oceanic spherules, and in legends of many people around the world ... While uniformitarianism remains true in respect of physical laws ... we must recognise unique events. Cretaceous is not a replay of Cambrian, or Edicarian . ... The Eons of Earth history are not uniform ... each has its own flavour. (p. 10, 11)

In the **"Imaginary One-off Big Bang" Theory** (sarcastically named by Fred Hoyle) about Earth's origin, Carey traces through Einstein and others to:

> Dirac (1937) whose model of the Universe ... triggered Gamov's meme that the Universe had an explosive beginning at a single point about 20 billion years ago .... What a massive point! One hundred billion galaxies, each containing ten billion billion stars condensed to a point!

The theory was received skeptically until 1964, but some rushed to join the believers after:

> Hubble's discovery of the universal cosmic recession, and the ... discovery of universal background radiation. (pp.3, 198,199)

(One cannot have the Universe expanding and the Earth remaining static in size).

The **Plate-Tectonics** meme emerged from the name-change about the 1960s

> ... because "continental drift", the name invented to discredit Wegener, was tarnished. (p.2)

Carey cites the standard meme of structural geology

> that orogenic belts are the sites of great crustal shortening and compression,

as due to Sir James Hall in 1815. He modelled

> folded strata with a stack of paper attributing his field observation to the cooling contraction of the Earth and so it is the meme to this day (p.37)

helped by the ready acceptance of Hall's idea by Hutton, Lyell, Dana, *et al.*

> Unfortunately, American and British certainty that they must be right has dominated the scene.

Thus the simultaneous development of the gravity-driven diapiric model of Earth by European geologists, listed by Carey from 1799 through the nineteenth century to 1943 and to Beloussov and colleagues in Moscow (p.37). One must ask whether the English-speaking establishment could continue to ignore this huge amount of evidence and escape the censure of those who now have massive data available from the Internet at the touch of a few keys.

There is too much evidence that Earth is expanding, according to the evidence for orogenesis, which is diapiric on a stretching crust. But, as Carey reminds us

> everybody "knows" that ocean floor subduction is a fact!

Was the 1815 'compression' and 'constant radius' of the Earth also a major factor with the 628-page summary of the radar imagery interpretation of Venus, published in August 1992 as volume 97, number E8, of the *Journal of Geophysical Research* and elsewhere?

Carey deplored that the writers

> ... sought in Venus what they believed to be Earth's history – an absolute faith in the plate tectonic model of an Earth of constant radius and compressional tectonics ... their creed blinded them to the fact that Venus' tectonics were the same as Earth's. ... If Venus had been studied in its own right fundamental progress could have been made in ridding Earth models of false concepts! ... for ... geology is part of the wider fabric of astronomy. (p.4-7)

He comments: *'It is not Venus that is odd, but our Earthly creed'*.

The **Lower Proterozoic Banded Iron Formation (BIF)** occurs on every continent in a narrow time slot at the end of the Archaean—never before or since—when wind became supreme for erosion and transport. Carey points out the special nature of this resource, totalling perhaps 10^{15} tonnes of iron ore, and, listing the 'sticking points', mentions that

> Nobody before me has suggested pan-global windstorms, which automatically satisfy all constraints". (p. 16)
>
> ... During the Early Proterozoic such dust storms several km deep would have become pan-global, like the dust storm which obscured the whole of Mars at the time of arrival there of Mariner 9, which even totally obscured the great volcanoes such as Olympus Mons.

On Earth the universal alternation of two very-different rocks ... was interrupted, staccato-like, by windstorm iron carbonate dust as the paper-thin laminae of the microbands, grouped in thicker mesobands, and these in greater megabands.

Carey asks how else occurred the precise correlation of even the microbands over great distances? How else the impulsive concentrations of vast tonnages of iron ore over such wide areas, when chemical restraints as Al and alkalis were almost nil and As, P and V all very low?

Also dealt with at length is Banket Gold (South Africa), Life, Glaciation, Granite, Ophiolite, Melange, Oroclines, The Benioff Zone, and Water.

Under **Earthquake and Eruption Prediction** Carey observes:

> vulcanologists and seismologists seek precursors that might give a few hours warning ... of calamity. Blot now offers hope of months of warning. He has studied hundreds of sequences with considerable success and some false warnings. ... Blot has pioneered a temporal succession from deep-focus earthquakes to shallow shocks and volcanic eruptions in the Solomon Islands through ... Vanuatu. (p.35)

Carey mentions the timely warning by Blot which allowed the evacuation of Tinakula Volcano by ship in 1965 before an eruption, and continues:

> The great August 1965 earthquakes ... were even more dramatic. On August 12 the New Caledonian Director of Messageries Maritime telephoned Blot because of his concern for his ship 'Le Tahitien' which had just tied up at Luganville on Santo, following Blot's earlier expectation of a great earthquake crisis. Blot replied that the risk was real and that a tsunami would almost certainly be generated that day. It could be dangerous for 'Le Tahitien' to be in shallow water in the narrow channel ... The director said that the passengers were going ashore. Blot advised to have them recalled immediately and get the ship out to sea. Blasts on the siren brought passengers running, the ship cast off and headed for the open sea – just in time. The Richter 7.7 earthquake struck, the docks cracked and subsided where the ship had been moored, and also the predicted tsunami came. (p.35)

Carey also mentioned the two Mount Etna eruption predictions in 1977 and 1982. The first was 340± 15days ahead, foreseeing a great lava eruption, the second 115± 15 days. The use of international earthquake lists for these long range warnings demonstrated what could be done.

The **"Himalayan Blunder"** Carey considers to be

> ... the greatest error of the last two centuries of geology ... the universal belief that the Himalaya was the site of colossal crustal compression. Everybody believed and most taught it ... It ranks with the Ptolemaic belief that the Earth was the stationary centre of the solar system. Both were wrong. Universal belief does not itself imply validity ... Geology must go back a century to the findings of Meyer and recognise that gravity governs tectonics ... (p. 37-52).

India has been part of Asia since Proterozoic or earlier time. India and Angaraland did not collide – the Himalayas could not have been born of collision or subduction, but from vertical uplift. Published sections of the Alps, Himalayas, and Appalachians are set side-by-side with the results of diapirism.

Evidence for **Expansion of Earth** has been given at three symposia and in two books (1976,1988), (p. 114-132). Reluctance to accept is because of

> the fundamental creed that folding and orogenesis are compressional. (p. 132)

But the earlier years of speculation are past. Actual measurements have been made

> using VLBI (very long base interferometry), and laser ranging to the Moon but in their interpretation they have assumed a constant-radius Earth ... (p. 127)

> The topological impossibility of plate-tectonic reconstruction (Meservey 1969) … is not a hypothesis, but an inescapable geometrical fact. (p. 115)

It means that plate-tectonicists must eventually recant .

Carey denies:

> … that cold surface lithosphere is being swallowed in the trenches at rates up to 20 cubic km per year. [If it were true] … not high heat flux, but several orders lower heat flux should mark the subducting fold belts. The subduction model cannot be correct [as it pairs] spreading ridges with trenches. It assumes that new crust added from mid-ocean ridges is balanced by old crust swallowed at the trenches. But the Mid-Atlantic ridge has no trenches along the Atlantic coasts anywhere. The American trench is on the PACIFIC SIDE of the continent. The nearest trenches to Europe are on the far Eastern PACIFIC side of Asia, where we find dilational small seas!
>
> Africa is worse, surrounded by rift zones (mid-Atlantic, mid Indian Ocean and Mediterranean). Within Africa there is no subduction sink which has swallowed an area of crust greater than the whole of Africa! No sink is there … only extensional rift valleys! Africa's "subduction" problem is "transferred" across the Atlantic and South America to the Pacific, and across Australia to the Kermadec Trench! Africa still has a problem to the south with Antarctica which is surrounded on all sides by its encompassing spreading ridge … Antarctica has no escape except via Earth expansion ….
>
> The Kermadec Trench is even worse — if that is possible! It is required to have swallowed 13,000 km of lithosphere (one-third of the circumference of the Earth!) during the past 150 million years. Yet some of the trench bottom is bare rock. Where are the 13,000 km of pelagic scrapings? … and the great andesitic volcanoes? All trenches investigated show horst and graben … [normal faulting! The fashionable Theory cannot meet its own subduction requirements!]
>
> No metamorphic rocks occur in trenches … glaucophane schists in orogenic cores are interpreted as former deeply subducted trench sediment, since regurgitated (p. 123-125)

Global Heat Flux is of a high order over spreading ridges and young fold belts. But plate-tectonic models assume a 30 km thick plate along a 30 000 km length of trenches being consumed at 2 cm/yr. Several orders of less heat flux are implied. The so-called Pacific Rim of fire cannot be explained by subduction into trenches.

Pangea reconstructions by several workers require that

> the roughly circular Pacific Ocean has increased its perimeter by more than 10,000 km while its area is reduced by 200,000,000 sq km … impossible on a constant-radius Earth. Some dare not see it, so they have to ignore it (p. 115)

For the **Solar System, the Moon and Asteroids**, Carey postulates a very different scenario for development. He also questions the assumption that water is an *abundant* constituent of all planets, and much else.

> There are as many horizons as there are mariners and there are as many Universes as there are observers to define them (p. 195)

A captain at sea sees another captain in a ship on his horizon, whose horizon extends as far beyond again. Billions of billions of galaxies are detectable in the cosmos. Some are large and some small, but they are strongly distributed about a mean. Why that size, instead of a billion times larger or very much smaller? Nobody seems to have asked that question. Carey tells why.

The **Cosmos** is a universal zero. In the first century B.C.,

> Titus Lucretius Carus wrote that nothing can be created out of nothing. Now, two thousand years later, orthodox science is no nearer to ultimate understanding. (p. 195)

In 1787 Kant wrote 'Igni de nihilo, in nihilum gemina posse' (nothing comes from nothing, nothing can revert to nothing) which Carey rephrased to 'Omnia de nihilo gemina nasci, in nihilum gemina posse reverti' (All things are created from nothing as mirror pairs, which pairs can revert to nothing). If ever there was a universal zero, then at all times the algebraic sum of all will remain zero. This is just touching on another of the many broad subjects.

Conclusion

Carey's book sums up his life's work. He will be remembered for his strength and courageous leadership in many issues of vital importance, but perhaps mostly for extending and maintaining the concept of Earth Expansion amidst the most formidable opposition from those unwilling to think the subject through—in the days when one was unable to quantify beyond speculation.

It was this which kept Expansion from becoming a main theory and perpetuated the teaching of one which was in itself incomplete, yet almost universally taught in earth science education as 'politically correct'.

However, one may now study the VLBI (Very Long Baseline Interferometry) terrestrial reference frame embedded radial vector component derived from NASA's Goddard Space Flight Centre's published geodetic VLBI Cartesian Values. These comprise 20 years of VLBI measurements of Earth's lateral and vertical change at 129 sites around the globe since August 1979.

These measurements are mentioned in Carey's book, (p. 127).

Carey hopes to bring a measure of sanity to less worthy elements in science. In this volume the very real aspects of tectonics have been so well explained that the young are now able to ask for answers of those who teach inadequately. Carey's book represents a staircase of knowledge,

> each step rising from its predecessor with addition of a fundamental new concept—a procession without having to recant.

This reviewer feels cut down to size by daring to touch so lightly on such enormous subjects, but the book holds pride of place in his library alongside other volumes by the same Author.

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*S. Warren Carey, AO, **1996**. Earth Universe Cosmos. University of Tasmania Press. 231 pp., 127 figs. qto. ISBN 0 85901 715 X. $Aus 45.00 incl. p. & p.*

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ABSTRACTS OF THESES

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AUSTRALIA'S GREATEST MINERAL DEPOSITS

EXTENDED ABSTRACTS OF THE 23RD ANNUAL CONFERENCE OF THE STATES' MINERALOGICAL SOCIETIES

BROKEN HILL, NEW SOUTH WALES, JUNE 2000

The following abstracts* are associated with the 23rd Annual Conference of the combined Mineralogical Societies of the various Australian States, held in Broken Hill in June, 2000. The theme of the Conference is epitomized in the above title. Eminent experts have agreed to speak on the geology, mineralogy and history of many important Australian deposits of international significance.

Of these, of course, Broken Hill itself is pre-eminent; a focus on "The Hill" is evident in the papers abstracted below. For this reason, if for no other, the setting of the Conference is significant. Reviews of the mineralogy of a number of major deposits are presented, as well as new science being announced for the first time in some instances.

The Conference has been supported by Pasminco Ltd and the City of Broken Hill. Their assistance is gratefully acknowledged. The Royal Society of New South Wales has agreed to the publication of the extended abstracts below as part of the Journal and Proceedings of the Royal Society of New South Wales. This is fitting in the sense that the Royal Society has in the past published many articles on Broken Hill, as well as other aspects of Australian mineralogy. The Royal Society of New South Wales is Australia's oldest learned Institution and its association with the Conference reflects its aims in promoting discourse on all aspects of scientific and cultural endeavour in Australia.

Professor Peter A. Williams
President, the Royal Society of New South Wales
President, the Mineralogical Society of New South Wales

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* Communicated to the Council of the Royal Society of New South Wales by Professor P.A. Williams

Mineral Occurrences in the Olary Domain, South Australia

P.M. ASHLEY

The Olary Domain forms part of the Curnamona Province, a large nucleus of Proterozoic rocks located in eastern South Australia and western New South Wales. The Olary Domain is contiguous to the Broken Hill Domain to the east and is dominated by metamorphic rocks of the Palaeoproterozoic Willyama Supergroup, together with significant amounts of Palaeoproterozoic and Mesoproterozoic intrusive rocks. Although large mineral deposits analogous to Broken Hill have not been discovered to date in the Olary Domain, there exists, nevertheless, a diverse range of mineralisation types, as well as metamorphic and metasomatic rocks, from which a wide variety of minerals, both common and unusual, may be obtained.

The Willyama Supergroup sequence in the Olary Domain displays regional correlations with that in the Broken Hill Domain, although there are numerous differences in detail. The lower part of the Olary Domain sequence is dominated by composite gneiss and migmatite. These rocks grade into the Quartzofeldspathic Suite. This contains the "Lower Albite" unit, dominated by ~1715–1700 Ma A-type metagranitoids and felsic metavolcanic rocks (Ashley *et al.*, 1996), the "Middle Schist", dominated by psammopelitic schist and composite gneiss, and the "Upper Albite", dominated by finely laminated albitite, as well as minor amounts of iron formation. The Quartzofeldspathic Suite grades up-sequence into the Calcsilicate Suite, dominated by laminated calc-albitites and minor calcsilicate and Mn-rich rocks. In turn, there is an up-sequence transition into the Bimba Suite, dominated by calcsilicate rocks and marble, locally with abundant Fe–Cu–Zn sulfides, and minor pelite and albitite. The Bimba Suite is overlain by a regionally sharp contact with the Pelite Suite, composed of pelite and psammopelite, psammite, tourmalinite and manganiferous iron formation (Page *et al.*, 1998).

Several intrusive suites occur in the Olary Domain and there have been at least five deformation and metamorphic events (Flint and Parker, 1993; Ashley *et al.*, 1997a). A-type granitoids were emplaced at ~1715–1700 Ma and co-magmatic rhyolitic volcanic rocks were erupted. Several small I-type granitoid bodies were emplaced into the central part of the Olary Domain at ~1640–1630 Ma. A major episode of deformation and amphibolite grade metamorphism occurred in the Olarian Orogeny at ~1600 ± 20 Ma, with subsequent emplacement of voluminous S-type granitoids and associated pegmatite bodies. Regional-scale retrograde metamorphism and alteration may have followed episodically between ~1580 Ma and ~1500 Ma, and there were further thermal perturbations during the Musgravian Orogeny at ~1200–1100 Ma. Mafic dyke emplacement at ~820 Ma was a precursor to development of the Adelaide Geosyncline and at least two episodes of low grade metamorphism and deformation occurred between ~500–450 Ma during the Delamerian Orogeny.

Regional-scale hydrothermal alteration has affected much of the sequence, as well as some intrusives, within the Olary Domain. Fluids have been high-temperature (~450°–600°C), commonly oxidizing and saline. They may have been derived by metamorphism of the host sequence, although there is a possibility of some magmatic fluid. Widespread metasomatism of.the Willyama Supergroup, and some of the intrusives, has occurred episodically between ~1630 Ma and ~1500 Ma, with development of Na–Fe assemblages (mainly albite ± Fe oxides, pyrite), with local strong Fe-metasomatism of iron formations and albitites and Ca–Fe(–Mn)-metasomatism of calcsilicate rocks (commonly in association with spectacular breccias), marble and quartzofeldspathic rocks.

Several styles of mineral deposits are recognised in the Olary Domain, including early syn-sedimentary or diagenetic types, various hydrothermal deposits related to intrusives, to metamorphic and alteration events, and to later weathering and redox-controlled processes (Ashley *et al.*, 1997b). Syngenetic and/or diagenetic deposit styles are represented by Fe–Zn–Pb sulfides in the Bimba Suite, iron formations and barite in the Quartzofeldspathic Suite and Mn-enrichments in the Calcsilicate and Pelite Suites. Manganiferous iron formations in the Pelite Suite are closely analogous to iron formations associated with the Broken Hill ore bodies. In the Bimba Suite, stratiform laminated to massive and disseminated sulfides are common in calcsilicate, marble and pelitic rocks and have given rise, in part, to extensive, base metal-anomalous gossans. Epigenetic mineral deposits are represented by various types of hydrothermal replacements, vein/stockwork systems, and rare metal pegmatites and U–Th–REE deposits related to the ~1600 Ma S-type granitoids. Supergene oxidation and diagenetic processes from the Mesozoic to Recent has led to Cu–Co–Au enrichment deposits and redox-controlled U and Au deposits, especially to the north of the outcropping Olary Domain.

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The Iodine Puzzle at Broken Hill

BILL BIRCH

Almost from the time of discovery of the Broken Hill lode, the richness of iodine in the Broken Hill oxidized zone became apparent. Not only were large masses of silver iodide found, but a strong iodine smell was also reported when mining operations broke into cavities rich in the iodine minerals.

The main iodine-bearing mineral is the hexagonal polymorph of silver iodide, iodargyrite. It was found in rich patches in the upper levels of the oxidized zone, especially in the Proprietary Mine, and also in the Australian Broken Hill Consols Lode, a few hundred metres to the east (Birch, 1999). In the main lode, iodargyrite occurred in two main environments. In the outcropping portion, or gossan, iodargyrite was found with other minerals such as chlorargyrite, cerussite and smithsonite, in cavities in secondary manganese and iron oxyhydroxides. In the complex oxidized zone below the gossan, iodargyrite was concentrated in masses of kaolinite containing other silver and mercury minerals.

Minor to rare amounts of other iodine-bearing species have been found at Broken Hill, most notably in the series marshite-miersite (cubic CuI-AgI), whose crystals are small and rare. Small amounts of iodine are present in minerals of the chlorargyrite-bromargyrite series, and in the complex mercury silver sulfide halide species such as perroudite and capgaronnite.

Despite the abundance of iodine in the secondary zone, and the existence of several synthetic polymorphs of silver iodide, only iodargyrite and its cubic polymorph miersite have been recorded. Also, despite the aridity of the region, no minerals containing iodine in a higher oxidation state (iodates) have been found. The structural, geochemical and temporal complexity of the Broken Hill oxidized zone makes it impossible to model the distribution of iodargyrite and groundwater. It appears that the concentrations of iodide ions in groundwaters were anomalously high, but there are no data on these concentrations.

It is postulated that AgI precipitated in the oxidized zone from solutions containing excess iodine. These solutions became concentrated by evaporation accompanying capillary action with a fluctuating water table. The richness of iodargyrite in kaolinite masses suggests the clay mineral had properties which effectively lowered the solubility of AgI. It is likely that there has been episodic precipitation of silver iodide in the oxidized zone during climatic fluctuations over the past few hundred thousand years or more, although the exact timing is unknown. There are two main sources possible for the iodine. The first is the sulfide ore itself, which is known to contain trace amounts of the element, probably in either the galena or in silver-bearing tetrahedrite. It is not known whether the iodine is incorporated in the sulfide lattice or is present in fluid inclusions. The other possible source is from seawater which originally filled the so-called ‘Murray Sea’ (now the Murray Basin). Windblown spray, or possibly seaweed built up around ancient shorelines, may have provided a source of iodine for groundwaters to concentrate.

There are other occurrences of iodargyrite in or adjacent to the Murray Basin region. At the Iodide mine at Mineral Hill, north of Condobolin in New South Wales, iodargyrite occurred in the oxidized zone above primary silver-lead-zinc sulfides. At Lake Boga, near Swan Hill in Victoria, a few small crystals of iodargyrite have been found on supergene copper sulfides in granite. Elsewhere in Australia the mineral is almost unknown, so it appears there is a regional concentration in the Murray Basin. Weathering and erosion of the Broken Hill oxidized zone may have distributed iodine widely into the regional hydrogeological environment over millions of years.

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The Mount Lyell Mines, Tasmania

R. BOTTRILL

The Mt Lyell mining field is situated in the West Coast Range between Mt Owen and Mt Lyell, near Queenstown, in western Tasmania. The field comprises numerous workings, open cut and underground, on more than 20 separate orebodies, in an area of ~10 square km. The Mt Lyell Mine is one of the oldest significant mines in Australia and has been operating almost continually for nearly 120 years. The mines have produced about 1.5 Mt of copper, 50 t of gold and 850 t of silver from some 130 Mt of ore in their lifetime and, despite a chequered history, the present owners talk of the mine continuing for another fifty years or more (a vast age compared to most modern mines). The mine is mineralogically most important as the co-type locality for the rare copper-iron-tin sulfide mawsonite, named after Sir Douglas Mawson, the Antarctic explorer and geologist. However, many other rare minerals are also recorded from these mines, including betechtinite, florenceite, svanbergite-woodhousite, stannoidite, hessite, jalpaite and stromeyerite. At least 85 species have been reported from the mines, many being found as attractive specimens.

The first lease in the field was on the Iron Blow, an ironstone outcrop at the head of the Linda Valley, pegged for gold in 1883. This mine struggled as a gold mine for several years, until Bowes Kelly and William Orr, both successful investors from Broken Hill, tested samples at the Broken Hill smelters and showed they were buying a copper mine. The mining engineer Robert Carl Sticht (for whom stichtite was named) was brought over from America in 1895. He developed the revolutionary pyritic smelting process which turned the economics of the mines around, and was the most important metallurgical process for sulfide ores until the development of sulfide flotation at Broken Hill.

The Mt Lyell copper-silver-gold deposits are best considered as Cambrian volcanogenic sulfides partly remobilized by Devonian hydrothermal fluids (Solomon *et al.*, 1987; Arnold and Carswell, 1990). The mineralisation is mostly hosted by schistose, highly altered rhyolitic to andesitic lavas and tuffs of the Cambrian Mt. Read Volcanics, with minor occurrences in Ordovician conglomerates and limestones, and is controlled by the intersection of two major faults. The mineralized zone is up to about 800 m thick. There are five major styles of mineralisation:

1. massive pyrite-rich bodies, with colloform textures and high grade copper, gold, arsenic and silver-rich shoots, postulated to have formed at or near the Cambrian seafloor;
2. banded, thin, pyrite lenses with chalcopyrite, galena and sphalerite (volumetrically very minor), also generally considered to be deposited near the Cambrian seafloor, like many volcanogenic massive lead-zinc deposits (*e.g.*, Rosebery, Hellyer);
3. disseminated, low to moderate grade, chalcopyrite and pyrite (the major ore type in recent years), is highly deformed and also generally considered to be Cambrian in age, probably formed during early sub-seafloor alteration of the volcanics;
4. higher grade bornite-rich ores along the Great Lyell Fault appear to have been remobilized during Devonian syn-deformational, fault-related hydrothermal events, very common in Western Tasmania and often associated with Sn-W-Bi-Pb-enriched Devonian granites;
5. "copper-clay" deposits containing native copper, cuprite, chalcocite and other sulfides in clays derived from deeply weathered argillaceous Ordovician limestones. The origin is not clear but could be either related to Devonian hydrothermal activity, or Ordovician to Recent weathering.

High grade ore shoots in the massive pyrite bodies were the original ores mined (after working of the gossan cap for gold), particularly in the Mt Lyell (Blow) and South Lyell Mines. These shoots contained pyrite, chalcopyrite, tetrahedrite, tennantite, stromeyerite, jalpaite, arsenopyrite, molybdenite, enargite and 2-3 ppm gold. Gangue minerals include quartz, barite, haematite, sericite and pyrophyllite. The banded pyrite ores contain grades of up to 28% lead and 20% zinc. The disseminated mineralisation constitutes the principal ores mined in recent decades, particularly from the Prince Lyell Mine. The ores contain pyrite, chalcopyrite, and minor tennantite, molybdenite, galena, sphalerite and bornite, with traces of other sulfides, tellurides and selenides. The ores grade about 1-2% copper, 3 ppm silver and 0.3-0.4 ppm gold. Gangue minerals, in approximate order of abundance, include quartz, muscovite, chlorite, siderite, magnetite, haematite, rutile, pyrophyllite, apatite, barite, fluorite, calcite, ankerite, zircon and monazite. Bornite-rich mineralisation is characteristic of the North Lyell area but is somewhat variable in nature. The ores grade about 4-8 % copper, 30-50 g/t silver and 0.4-1 g/t gold. Ore minerals include bornite, chalcopyrite, pyrite, chalcocite, tennantite, galena, betechtinite, mawsonite, digenite, sphalerite, molybdenite, linnaeite, and stromeyerite. Gangue minerals are as above, but cherty quartz, barite, fluorite and haematite are typically more abundant. The "copper- clay" deposits are locally very copper rich but have only constituted a small part of production to date. They contain native copper, cuprite, chalcocite, digenite, bornite, covellite, chalcopyrite, galena, sphalerite and goethite in illite-kaolinite clays.

Massive chalcopyrite and bornite samples may be quite coarse and colourful, but most of the rarer minerals are microscopic. Gossans were poorly developed due to glaciation and erosion, but some good malachite occurred in them. Good copper and cuprite crystals occur in the "copper- clays," but most good collectable minerals (crystalline, mm to cm sized) occur within late, open veins and fractures, and include albite, barite, calcite, chalcopyrite, chlorite, cuprite, dolomite/ankerite, fluorite, fluorapatite, haematite (specular), pyrite, quartz (large crystals, some with stunning haematite and chlorite inclusions) and siderite.

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Minerals of the Cobar Mining District

J.R. CHAPMAN

The Cobar district has been a significant mineral producer since the discovery of copper in 1870 at what later became the Great Cobar Mine. By the turn of the century the district had become one of Australia's main copper producing areas. Significant gold, lead, zinc and silver production is associated with several deposits. The geology of the area comprises deformed sedimentary sequences of Early Palaeozoic age. Mineral deposits typically form steeply plunging sulfide lenses that extend to great depths. There has been much debate on the origin of the deposits but it is generally accepted that most formed from deep basinal hydrothermal fluids focussed along regional structures.

Primary sulfide minerals in the deposits include abundant pyrite, pyrrhotite, chalcopyrite, galena and sphalerite, with lesser amounts of tennantite, tetrahedrite, enargite and arsenopyrite. Cubanite is a common accessory and bismithunite is found in minor amounts in many of the deposits (Rayner, 1969). There was very little open space in the primary ores and, except for euhedral cubes of pyrite, sulfide minerals are mostly massive. The CSA Mine has produced well crystallized specimens of pyrite forming lustrous cubes to 1 cm and rounded aggregates to 15 cm in size. Rare chalcopyrite crystals to 3 cm, and small, unusual, acicular crystals of cubanite have also been collected at this mine. Secondary minerals derived from oxidation of primary sulfides are common on the field; weathering commenced in the Cretaceous to Middle Miocene period (97-16 Ma) and has continued to the present (Leah, 1996). The following occurrences are noteworthy.

Fine examples of azurite ($Cu_3(CO_3)_2(OH)_2$) were collected from Great Cobar, Gladstone and Mount Hope Mines. Recent mining at Girilambone exposed beautiful specimens of well-formed and lustrous crystals to 4 cm and stacked aggregates to 7 cm in length. Malachite ($Cu_2CO_3(OH)_2$) is ubiquitous in the copper deposits and was best represented in the Great Cobar Mine where it occurred as masses of acicular crystals forming velvety to dense laminar coatings and crusts.

Beautiful cone-shaped aggregates to 2.5 cm in length showing silky chatoyantcy were collected from the Great Cobar Mine and similar specimens are noted from the Nymagee Mine.Very fine examples of complete or partial pseudomorphs of malachite after azurite are common, particularly from Great Cobar and Mount Hope.

Native copper (Cu) forms thick, arboresent to delicate, dendritic masses, sometimes with well-formed crystals, particularly at Cobar and Mount Hope Mines. Cuprite (Cu_2O) is often associated with native copper as coatings or small octahedral crystals. Carne (1908) reported that it occurred at the Great Cobar Mine in '*massive bunches of great purity near the surface*' while Andrews (1913) claimed it to be common in all copper mines at groundwater level. The acicular form, *chalcotrichite*, was also encountered in the mines at Cobar. Copper phosphate minerals are prominent in some deposits. Mammillary masses of pseudomalachite ($Cu_5(PO_4)_2(OH)_4$) from the West Bogan Mine near Tottenham are among the finest examples of this mineral in the world. Pseudomalachite was abundant at Girilambone as crusts and coatings on gossan and other minerals, intergrown with malachite, as replacements after libethenite and as very small sprays of emerald green crystals showing an unusual helictite-type structure. Also at Girilambone, libethenite ($Cu_2PO_4(OH)$) occurred as light to dark green, stubby, prismatic and tetragonal bipyramidal crystals 1-6 mm in size, abundant in the upper parts of the oxide zone.

In the Elura lead zinc silver deposit, a zone of supergene enrichment that averaged 0.3% Ag was mined during the 1980s. This zone provided a treasure of mineral specimens.

Native silver (Ag) was abundant, occurring mostly as fine, delicate groups of small crystals dispersed through gossan. In places it formed spongy masses to thick dense wads many kilograms in weight. Coarser elongated crystals commonly referred to as wires were common, ranging up to 200 mm long and 5 mm thick. Mimetite ($Pb_5(AsO_4)_3Cl$) was the most prominent lead mineral. Larger crystals formed yellow to green, barrel-shaped hexagonal prisms, tending to flatter hexagonal prisms with increasing size. Spectacular specimens of large green crystals to 2.5 cm in length are among the best in the world. Cerussite ($PbCO_3$) occurred as delicately reticulated specimens or as crystals, often exhibiting a sixling habit. Native silver crystals grown on cerussite were reasonably common, an unusual association also noted from the CSA Mine.

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Greenbushes: a 19th Century Mine Producing 21st Century Minerals

PETER CLARK

The Greenbushes rare-metal pegmatite in Western Australia is unquestionably deserving of inclusion in any list of Australia's greatest mineral deposits; its size, complexity, mineralogical diversity and production make it a world class mineral deposit. It is situated some 300 km south of Perth and 80 km SE of the Port of Bunbury and lies in the Western Gneiss Terraine of the south-west portion of the Yilgarn Block. The deposit is one of the world's largest lithium and tantalum resources. Currently the mine produces about 20% of the world's tantalum and is the world's largest lithium producer. Production has been continuous for over 100 years and reserves of tantalum are sufficient at the current mining rate to last a further 17 years. The pegmatite is notable for the occurrence of tantalite and spodumene as well as the rare tantalum minerals stibiotantalite, holtite, microlite, tapiolite, and wodginite (Hatcher and Clynick, 1990). The rare amphibole holmquistite (lithium glaucophane) is found in the exocontact zone (Witt, 1990).

Cassiterite was found in the area by a kangaroo hunter D.W. Stinton in 1888, although the Government Geologist E.T. Harding had a role in the discovery. Mining commenced in 1888 with tin being produced since that time. Early operations were small scale and in 1893, as a result of tin smelting problems, the presence of stibiotantalite and tantalite was confirmed. It was not until 1944 that markets for tantalum were established. More recently, tantalum and lithium have become the major revenue earners. In 1949, spodumene was identified by the Geological Survey of Western Australia in a specimen collected in 1928 and previously identified as feldspar. Until 1970 most production came from alluvial deposits and small underground and open pit operations. At that time, Greenbushes Ltd amalgamated all of the small mining tenements on the field and began production from the weathered pegmatite. Price increases in the late 1970s saw increased production and exploration in the weathered zone and the world significance of the deposit became apparent. Between 1977 and 1980, deep exploration drilling confirmed an extensive primary deposit below the weathered zone. The complex nature of the pegmatite was revealed and enriched Sn-Ta and Li zones were delineated. In 1990 Gwalia Consolidated Ltd took control of the operations of Greenbushes Tin and Lithium Australia; Sons of Gwalia Ltd are the current operators.

The Greenbushes pegmatite is part of a dyke swarm some 7 x 1 km in size intruded along a NNW shear zone within the Balingup Gneiss Complex (Witt, 1990). Pegmatites have intruded a sequence of metasediments and metabasic igneous rocks. The longest body, about 3.3 km long and up to 250 m wide, has been drill-tested to a depth of 500 m. The pegmatites dip at 40° to 50° W. Contacts are sharp but comprise mylonite zones while xenoliths occur within the pegmatites, which have been recrystallized with a grain size of generally less than 1 mm. Gneissic textures with mineral banding are common. It is evident that the genesis of the deposit is complex as is clearly shown by the multiple intrusion of pegmatite and dolerite dykes along a reactivated shear zone.The pegmatite is zoned and contains three internal asymmetric zones along with a discrete contact zone (Table 1).

The mineralogy of the deposit has been described by a number of workers (East, 1894; Simpson, 1952; Pryce, 1971; Pryce and Chester, 1978). Simpson (1952) described the occurrence of stibiotantalite ($SbTaO_4$) in detail and made the point that the mineral was found only in small quantities and in fragments generally < 3 cm in diameter. East (1894) described stibiotantalite thus: "*the mineral is essentially a tantalate of antimony, part of the tantalic acid being replaced by niobic acid and part of the antimony oxide by bismuth oxide.*" The mineral was described by the alluvial miners as "resin tin" and was a deleterious component of the ore. Pryce (1971) described the new mineral holtite ($Al_6(Ta,Sb,Li)[Si,As)O_4]_3BO_3(O,OH)_3$) occurring with tantalite and stibiotantalite. Both stibiotantalite and holtite form pseudomorphs after tantalite.

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Table 1. Zoning of the Greenbushes Pegmatite

Unit	Major minerals	Accessory minerals	Geochemistry
exocontact	biotite, holmquistite	tourmaline, garnet, arsenopyrite	Li (As)
contact	albite, quartz, Tourmaline	garnet, apatite, muscovite; Sn, Ta, and Nb oxide minerals	Na (Sn, Ta, Nb)
K-feldspar	quartz, microcline	tourmaline, spodumene	K. Rb (Cs) (B, Li)
albite	albite, quartz, tourmaline, Muscovite	apatite, spodumene; Sn, Ta, and Nb oxide minerals	Sn (B, Sn, Ta, Nb, Be)
spodumene	spodumene, quartz	albite, apatite	Li, Na (P)

The Nature and Significance of Colloform Textures in the Pernatty Lagoon Copper Deposits, South Australia

ROBERT A. CREELMAN

The most significant of the Pernatty Lagoon copper deposits occur along a major disconformity within Adelaidean rocks of the Stuart Shelf, a subdivision of the Adelaidean Supergroup. Adelaide Supergroup rocks form a middle to late Proterozoic apron around the older and deformed Gawler Craton The sediments were derived from the crystalline basement of the Gawler Craton to the west, but the Mt Painter and Willyama Inliers to the north-east were sources that made contributions to later rock units. Graben structures provided deep basins which accumulated thick blankets of sediment throughout Adelaidean time. On the Stuart Shelf the sediment wedges were thin following the deposition of the relatively thick Willouran Pandurra Formation. Post Pandurra Formation units lap onto the Pernatty 'Culmination', a major paleostructural high on the Stuart Shelf. The Cattle Grid orebody was the most significant of the deposits. The sulfides occurred along a disconformity between the Pandurra Formation, a quartzite, and the Whyalla Sandstone. There is evidence in other areas that breccias and disconformities – open spaces in the rocks, localize the mineralisation. A full description of the geology and the ore deposits can be found in Creelman (1984) and Tonkin and Creelman (1990).

Metal sulfides that deposit in the body of the rock can be early in the rock history, before diagenesis, or later than diagenesis. Whether consolidated or unconsolidated, deposition in a rock body requires open spaces, or if open spaces are not available, then the depositing minerals must create space for themselves. The accommodation can be accomplished in three ways:

1. the mineral grows in open fissures or cavities in the rock. The process is called 'secretionary growth' (Ramberg, 1952);
2. the mineral grows in a space by pushing aside other minerals as it crystallizes. The process is called 'concretionary' growth (Ramberg, 1952);
3. the mineral grows by replacing an older mineral or cluster of minerals occupying space in the rock mass. This is chemical replacement *sensu stricto*.

Although it is possible to isolate one of the three processes as dominant in any depositional situation, clearly all three can operate simultaneously and some situations are the product of the combination in whole or in part. There are many good examples of minerals that fill spaces in the Pernatty Lagoon copper deposits. The interstitial sulfide minerals in the arenites, vughs coated by sulfide crystals, and the colloform textures in the Pernatty Lagoon ores are all notable examples. Other examples are the carrollite-arseniferous pyrite spheroids, marcasite rosettes, and framboidal pyrite. It is the colloform textures that are of special interest in the Pernatty Deposits.

Colloform texture is defined as rounded reniform masses of mineral which result from colloidal precipitation. Ramdohr (1969) writes that according to the laws of physical chemistry all colloidal precipitates are metastable with a tendency to crystallize. This manifests in the loss of water as crystallization proceeds, perhaps with later increase in grain size and an exsolution-like precipitate of other minerals. Ramdohr notes that sphalerite and milnikovite-pyrite are the most common sulfides exhibiting colloform textures, although rotund and spherical forms of minerals, banding accompanied by syneresis cracking and pellet or oolitic structures are relatively common in oxides of iron, manganese and aluminium. Ramdohr's ideas are based on work by Rodger (1917) and Grigoriev (1928) who included all reniform shapes made up of fine crusts, spheroids, vesicular, bubble-like masses, concentrically banded radial spheroidal masses, and devitrified masses of various forms dominated by concentric or reniform structures. Grigoriev extended the definition to Liesegang rings and shells that included solid material more appropriately classified as concretionary growth.

The above ideas have left an indelible mark on the definition of what is colloform as it was a self-evident truth that colloform textures indicated the involvement of a colloid or gel stage during deposition. Roedder (1968) systematically examined the many textural criteria used to argue for gels and found them to be either ambiguous or invalid. Roedder considered that the dominant parameter controlling colloform texture formation is a high degree of super-saturation that results in many points of nucleation and rapid crystallization. The result is many small crystals coated on a flat surface, rather than a few large crystals that grow in the depositing fluid. Super-saturation is easy to achieve in solutions of substances that have low solubilities.

The balance between conditions that produce fine banding and those that grow large crystals is delicate. Roedder postulated that a flowing fluid becoming more saturated as it moved through a conduit could grow crystals, but stagnant solutions at very high levels of super-saturation produce colloform layers. It is noteworthy that large chalcocite crystals are directly associated with colloform textures in the Cattle Grid ores, which implies that conditions of colloform deposition have given way to those that produce crystals. The change from colloform deposition to crystal growth deposition is, using Roedder's criteria, indicative of changing hydrological conditions from stagnation to flow.

A change from one mineral phase to another in the fine bands is indicative of changing geochemical conditions. The majority of the bands seen in the Pernatty Lagoon ores are sulfur-rich bornite and chalcopyrite that represent low redox conditions relative to chalcocite (Garrels and Christ, 1965; Creelman, 1984). Redox levels are possibly the most variable parameter in the Pernatty groundwaters and are directly related to the activities of HS^- and S^{2-} in the solutions. At ambient temperatures the only demonstrated mechanism that produced sulfides is biogenic reduction of sulfate. Lambert *et al.* (1971) found sulfate-reducing bacteria in all groundwaters around Pernatty Lagoon, including the hypersaline playa lake waters themselves. An explanation of the banding must therefore involve variations in biogenic activity. Biogenic sulfate reduction is controlled by the supply of nutrient to the bacteria and, if the system is closed with respect to sulfur, it is possible that depletion of sulfur or oxygen will result in progressively lower levels of sulfide production, which can be redressed by recharge. It is then possible to have a series of bacterial blooms and decays which result in either excess sulfide or depleted sulfide supply.

The recharge is the temporal control. Roedder favoured the change in hydro- geochemical conditions as due to the annual fluxing of groundwater recharge, which would bring new nutrient and perhaps redistribute depleted elements and radicals. He consciously used the term "varve" to describe the bands. Annual recharges are not necessarily the only mechanism. Longer term aquifer recharges, *e.g.*, one in ten, twenty or even one hundred years are all possible redistribution-resupply events. What is necessary is the temporary removal of stagnation conditions in the groundwaters, *i.e.*, to periodically open the system.

The significance of colloform textures at Pernatty Lagoon is that they represent remobilization and redeposition of copper-bearing sulfides under special geochemical conditions. Normally, redeposition of copper-bearing sulfides results in covellite, but in the case of the colloform textures redox levels have been low enough to redeposit iron as well as copper. Such conditions can only be the result of active bacterial reduction in aqueous media. It is postulated that changing redox conditions, reflected by bands of different sulfide phases, represent blooms and decays of biogenic activity. Above all, colloform banding is the product of supersaturation in the aqueous media under hydrological conditions that are at, or approach, stagnation and the texture is evidence for 'supergene' enrichment under active reducing conditions. The fine banding is particularly fragile as copper and copper iron sulfides re-equilibrate, recrystallize and are easily replaced with only minor changes in physical and chemical conditions. The texture is consequently rare and only seen in ore deposits where the processes are close to or contemporary.

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The Origin of Fault Zone Minerals at Broken Hill, New South Wales

ANDREW GALLACHER & IAN PLIMER

The Palaeoproterozoic Willyama Supergroup comprising metasediments and meta-igneous rocks, is the host to the overturned Broken Hill orebody. The orebody underwent a number of distinct events of coeval deformation and metamorphism in the Palaeoproterozoic and metamorphism and deformation at 520 Ma. The orebody has a long history of both prograde and retrograde sulfide deformation, metamorphism, retexturing and new mineral formation. Late stage brittle deformation took place well after the 520 Ma event, probably in the Mesozoic or later (Stevens, 1999).

The brittle deformation zones, which transgress the orebody, are planar and vary from millimetres to metres in width and displace the Broken Hill orebody. The carbonate-rich fault zones commonly bifurcate, rarely contain vughs lined with terminated crystals in cavities metres in length and contain a diversity of clasts of high metamorphic grade sulfide rocks. The fault planes are strongly slickensided. The fault zones act as an aquifer and, closer to the surface, fault zones contain goethite, rare gypsum and supergene clay minerals.

The fault zones are mineralogically unusual because they contain no lead or zinc minerals yet are enclosed by a 280 Mt massive lead-zinc orebody. Furthermore, the Broken Hill orebody is unusual when compared with other massive sulfide deposits because it contains a paucity of iron sulfide minerals. By contrast, iron sulfide minerals are common in the fault zones. The fault zones have produced spectacular samples of manganoan calcite, kutnahorite, rhodochrosite, neotocite (*sturtite*), chlorite, inesite, fluorapatite, alabandite, pyrite, marcasite and amethystine quartz. There was a sequential deposition of minerals in the fault zones (Plimer, 1982).

Electron microprobe analyses of blocky, fibrous and terminated fault zone carbonates shows that there is a great variation in the Mn content of carbonate minerals. In places, this variation is repeated over a number of cycles. Fault zone minerals contain very small necked-down fluid inclusions along cleavage planes.

Attempts to date the fault zone apophyllite using Rb-Sr techniques failed. Recalculation of the model ages shows that mixing probably did not take place and, although fluorapophyllite is commonly the last phase precipitated in vughs, it is poorly Sr retentive. Loss of Sr was probably due to a long history of fluid flushing along fault zones. The high initial Sr values (0.811-0.872) for fault-zone carbonates compared to carbonates in the enclosing orebodies (0.716) suggests that fault zone carbonates derive from metasediments and that the fault zones are not in isotopic equilibrium with the orebodies.

Sulfur isotope studies on the Broken Hill orebody show a great consistency with a cluster around 0 per mil. Mylonite zone-hosted Thackaringa-type deposits emplaced at 520 Ma also cluster around 0 per mil. Pyrite from the fault zones is extremely isotopically negative suggesting kinetic fractionation of sulfur isotopes or highly fractionated sulfur isotopes derived from biological material. Carbon and oxygen isotope analyses of fault zone carbonates show extremely light carbon and variable but overall light oxygen. The carbon and oxygen isotope values of fault zone minerals are unlike the carbon and oxygen isotopes in the enclosing orebody.

It is concluded that the components in the fault zones at Broken Hill did not derive from the enclosing Broken Hill Pb-Zn orebody. On the assumption that the fault zone hydrothermal minerals formed from ascending and not descending fluids during and after brittle deformation, the source of the light stable isotopes can be determined. Because the Broken Hill orebody occurs on the downward facing limb of a recumbent fold, the upper part of the Willyama Supergroup stratigraphy has been beneath the orebody since Palaeoproterozoic folding. The uppermost part of the Willyama Supergroup is the Paragon Group, a sequence of carbonaceous (and rarely sulfidic) pelites with rarer psammopelites, pelites and calc-silicates. The carbonaceous and sulfidic material of the Paragon Group is of biological origin.

It is concluded that there was an episodic flushing of low temperature reduced carbon- and sulfur-bearing fluids up faults from the underlying Paragon Group in Mesozoic or younger times. Fault zone minerals were precipitated from fluids undersaturated to saturated in carbon dioxide; fluids associated with the final phases of mineralization were strongly acid. If any components in the fault zone could have derived from the enclosing Broken Hill orebodies, then it is possible that the minor amounts of manganese and fluorine in the fault zones may have derived from fluid-sulfide rock interactions.

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The Occurrence and Origin of Gold Nuggets in Victoria

DERMOT HENRY

Victoria has produced in excess of 2500 tonnes of gold (some 80 million ounces) since gold mining commenced in 1851. Exceptionally rich alluvial deposits attracted hopeful prospectors from overseas to the newly founded Colony in the early years of the rushes; later, quartz reef mining prolonged the industry. The occurrence of large gold nuggets throughout the alluvium provided the greatest fascination on the goldfields. Many large nuggets were discovered on or close to the surface while others occurred in buried auriferous alluvium in "shallow" or "deep leads". The allure of discovering a nugget and gaining instant wealth sustained many prospectors. Dunn (1912) noted however, *"there is a tragic side to nuggets also, for in the early digging days the sudden acquisition of more or less wealth in the form of a nugget* *often caused the mind of the finder to become unhinged".*

The Victorian goldfields have produced more and larger gold nuggets than any other goldfield. *A List of Nuggets Found in Victoria* published by E. J. Dunn (1912) listed some 1327 nuggets ranging from the largest, the Welcome Stranger, weighing some 2520 ounces down to nuggets of the order of 20 ounces. The *List* is not regarded as complete. In recent years with the ready availability of metal detectors nuggets continue to be unearthed with several examples greater than 200 ounces brought to popular attention.

Since the earliest discoveries of nuggets numerous theories were suggested to explain their origin. The theories polarised into two camps:

1. the nuggets were derived from adjacent auriferous quartz reefs.
   The proximity of many large nuggets to reefs was viewed as compelling evidence that they had been derived from these reefs. Many nuggets also contained large fragments of angular quartz or indentations from quartz crystals;
2. the gold had precipitated *in situ* from groundwater. Gold precipitated in timber found in deep leads or associated with pyrite which had replaced roots, branches and stems of recent trees was regarded as proof of the occurrence of gold in meteoritic waters (Newbery, 1868; Smyth, 1869). The purity of the nuggets in comparison to small fragments of gold in the reefs and the scarcity of large masses of gold within the reefs were also cited as evidence that the nuggets had formed *in situ*.

Supergene gold has been recorded from numerous deposits around Australia and overseas (Wilson, 1984; Boyle, 1979). Some gold nuggets from the Coolgardie region Western Australia contain concretionary iron oxides "limonite." The gold completely encloses the nodules and the iron oxide nodules contain finely disseminated gold. This has been cited as evidence that these nuggets accreted in the deposits and are associated with laterite horizons. Other nuggets in this field are intimately associated with quartz reefs.

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Mineral History of the Mount Morgan Copper-Gold Deposit, Queensland

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The Mount Morgan pyritic copper- gold deposit, 37 km south-south-west of Rockhampton in central eastern Queensland, was discovered in 1882 and over the ensuing eighty years produced 199,000 kg of gold and 295,900 tonnes of copper metal. The deposits occur within a sequence of rhyolites, diverse volcanoclastic sediments, jasper, chert, lava and limestone blocks and crystal-rich pumiceous breccia. These constitute the Mount Morgan Mine Corridor Volcanics which are divided into five units: Upper Mine Sequence, Banded Mine Sequence, Middle Mine Sequence, Lower Mine Siltstones and Lower Mine Sequence. These acid volcanics and their derivatives form the lower part of the mid-Devonian Capella Creek Group. The volcanics are intruded by the polyphase Mount Morgan Tonalite comprising tonalite, trondhjemite and quartz gabbro of about 380 Ma in age. The regional and local geology of Mount Morgan is quite complex with numerous differing accounts evident in the literature. The most comprehensive studies are those of Messenger and Golding (1996) and especially Messenger, Golding and Taub (1997).

The area is heavily faulted and the volcanics are further intruded by porphyries coeval with the acid volcanics and, in part, were emplaced in still wet sediments *i.e.*, synsedimentary intrusions (Golding *et al.*, 1993). The rocks of the Mount Morgan area, including the orebody, were then invaded by a series of conjugate dykes (NE-SW and NW-SE) of Triassic age with further faulting.

Two differing genetic models have been presented as to the origin of the Mount Morgan orebody: (1) a structurally controlled breccia pipe with some replacement with ore derived from the intruding tonalite (Cornelius, 1967, 1969; Staff, Mt. Morgan Ltd., 1965), and (2) a volcanogenic massive sulfide pipe deposit (Paltridge, 1967; Frets and Balde, 1975; Lawrence, 1977; Golding *et al.*, 1993).

Although evidence for a large-scale replacement is scant, the orebody is pipe-like in structure (somewhat resembling a boot) with much of the ore as large brecciated masses. Toward the top of the open cut is a remnant of a stratiform pyrite-barite unit within black shales and considered to be of submarine volcanic exhalative origin. The model proposed by Messenger *et al.* (1997) and the similar model by Lawrence (1977) tends to reconcile the volcanic-exhalative and the breccia pipe concepts as being parts of a submarine mineralization process where black smoker chimneys are eventually disrupted by an ultimate explosive episode which produced the transgressive breccia pipe. The source of the ore, in this model, would be the acid volcanics and the associated porphyry of the Mine Corridor rocks.

The deposit had an expansive gossan which was extensively prospected but found to be mostly barren. Within this gossan was a smaller ore-derived gossan lying above the breccia pipe. The ore was mined underground initially and then by open cut, partly because of a mine fire in the 1920s. The ore at Mount Morgan did not generate

Table 1. Distribution of primary minerals at Mount Morgan.

Mineral	Composition	Relative abundance
Pyrite	FeS_2	dominant
Chalcopyrite	$CuFeS_2$	major
Magnetite	Fe_3O_4	semi-major
Pyrrhotite	$Fe_{1-x}S$	semi-major
Marcasite	FeS_2	accessory
Gold	Au	accessory
Molybdenite	MoS_2	accessory
Digenite	Cu_7S_4	minor accessory
Chalcocite*	Cu_2S	minor accessory
Hematite	Fe_2O_3	minor accessory
Calaverite	$AuTe_2$	minor accessory
Petzite	Ag_3AuTe_2	minor accessory
Sylvanite	$AgAuTe_4$	minor accessory
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	minor accessory
Sphalerite	ZnS	minor accessory
Bismuthinite	Bi_2S_3	minor accessory
Covellite*	CuS	minor accessory
Galena	PbS	minor accessory
Arsenopyrite	FeAsS	minor accessory
Goethite	FeO(OH)	minor accessory
Cubanite	$CuFe_2S_3$	trace
Cassiterite	SnO_2	trace
Rutile	TiO_2	trace
Bismuth	Bi	trace
Bornite	Cu_5FeS_4	trace
Coloradoite	HgTe	trace
Hessite	Ag_2Te	trace
Silver	Ag	trace
Tellurobismuthite	Bi_2Te_3	trace
Tetradymite	Bi_2Te_2S	trace

*Mainly supergene.

many secondary minerals. Minor amounts of malachite and azurite were occasionally seen but little else though the gossan did provide some very colorful iridescent limonite. Thirty primary metallic minerals occur in the breccia pipe, Table 1 (Lawrence, 1974), but only pyrite, chalcopyrite and magnetite are readily visible macroscopically. Gold is rarely seen other than under the microscope as are most of the other minerals, many of which have been noted only once or twice. A particular feature of the pyritic ore is the differing textures ranging from aggregates of irregular grain shapes of very variable size (1 mm to 2 cm or so) to masses of granular sugar-like grains of a uniform 1 to 1.5 mm. The latter type is somewhat friable with individual grains having a polygonal shape.

It is evident that stress build-up, as a result of magma drag and compression resulting from sidewards spread during later dyke emplacement, affected the ore. Microscope study of a large number of polished sections shows that the granular pyrite has been annealed as has the associated magnetite, pyrrhotite and quartz. The pyrite of the irregular grain shape shows no such features.

In order to dissipate strain energy and to balance surface tensions, a movement of atoms in the grain exteriors occurs resulting in polygonally shaped grains whose sides, in two dimensions, are seen to meet in groups of three with triple-point junctions of 120^0 in single phases – in this case pyrite. A histogram of triple-point angles plotted against frequency for annealed pyrite from Mount Morgan gives a bell-shaped curve with a 120^0 maximum (Lawrence, 1972). Other features indicative of annealing such as the spreading of minor phases, such as chalcopyrite, along grain boundaries of major phases and to triple point junctions, and the spheroidization of minor phases in major phases *e.g.* pyrite in annealed quartz, are frequently observed under the ore microscope.

The effect of temperature elevation on a pre-existing ore subjected to strain has induced annealing–recrystallization within parts of the Mount Morgan deposit. Pyrite, which normally fails by brittle fracture, requires an extremely slow strain rate at relatively high temperatures to anneal; these conditions were operative at Mount Morgan. The particular influence of temperature elevation brought about by igneous intrusion into the already existing orebody has led to the concept of thermal metamorphism of a sulfide ore with Mount Morgan as an example.

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Minerals of the Harts Range, Northern Territory

DON McCOLL

The Harts and Strangways Ranges northeast of Alice Springs are parts of the Arunta Inlier, a group of Archaean age rocks which lie roughly east-west across Northern Territory just north of Alice Springs. In the more easterly sections, and particularly within the Harts Range, these rocks were originally intensely regionally metamorphosed to at least granulitic grade more than a billion years ago. Much of this alteration has however, been obscured by subsequent retrogressive changes, igneous intrusions, and an additional later profusion of pegmatitic, hydrothermal and metasomatic mineral veins introduced during relatively recent tectonism, perhaps only 300 million years ago. The mining history of the Harts Range area is quite insignificant, being limited to little more than prospecting and pitting of the pegmatites for mica during about thirty years in the early to mid-twentieth century. Many of the miners were first generation Italian immigrants, and they were aided in both prospecting and mining by the Aboriginal people of the Eastern Arrente tribal group. Even now the area is sparsely populated and pastoralism is virtually the only industry.

KORNERUPINE AND SAPPHIRINE

The geology of this deposit has been briefly described before (Warren & McColl, 1983; McColl & Warren, 1984). It consists of a single band within a quartzo- feldspathic gneiss which has been inter- laminated with mafic intrusives, which now appear as pyroxene granulites. The layer representing the host rock is believed to have been originally composed of felsic volcanics, tuffs and basalts in a section generally dominated by quartz-rich sediments, and all being about 1.8 billion years old. From the chemical composition and general local geology, it is suggested that the band might have originally consisted of soda-rich sediments deposited in a non-marine lagoon fed by hot volcanic springs. The formation of kornerupine and sapphirine, which are favoured by metamorphism at elevated pressure and temperature, infers that this band was downwarped to a depth, which may have been as much as 10 kilometres, about 1.5 billion years ago. This resulted in the formation of well shaped, eight sided prismatic crystals of kornerupine up to 20 cm in length and 5 cm diameter, and tabular crystals of sapphirine up to 3 cm in diameter and 1 cm thick. Later retrogressive alteration should have tended to destroy both of these minerals, but at this location and a few others in the Harts and Strangways Ranges, occasional cores of each pure mineral have survived within pseudomorphous idioblastic outlines.

CORUNDUM RUBY

Australian ruby was first recorded as well formed tabular crystals up to 5 cm diameter and 1 cm thick from a location south of Mount Brady in the Entia Creek headwaters of the Harts Range in 1978. The occurrence is restricted within and along the margins of irregular blocks of felsic amphibolite which are enclosed within schistose masses of dark green chloritic amphibolite. These host amphibolite blocks are best interpreted as former xenoliths or folded boudins of felsic aluminous amphibolite (anorthosite) which were incorporated, perhaps around a billion years ago, within ultramafic intrusive bodies having the probable form of sills or laccoliths (Lawrence *et al.*, 1987). Localised contact metamorphism of many of these xenoliths/ boudins would account for the formation of corundum, which would have the ruby colouring imparted by permeation of chromium from the ultramafic. Some of these crystals were exceptionally large, being as stated, up to 5 cm in diameter. They generally tended to a flat tabular habit however, with very short *c*–axes. Subsequent retrogressive alteration tended to develop sericitic and fuchsitic coatings on many of the crystals, and tectonic deformations have been noted, which may principally be ascribed to the later period of the Alice Springs Orogeny about 300 million years ago. Mining of this deposit was carried out during the late nineteen-seventies and early eighties, and although a considerable total weight of ornamental ruby was obtained, most of it was used to make cabochon gemstones, and virtually none of it was up to facetting grade. Operations were discontinued after about three years, and only minor work has been done at the site since.

SCEPTRE QUARTZ CRYSTALS

Large prominent veins of pegmatite and quartz, sometimes containing characteristic minerals such as muscovite, tourmaline, beryl, calcite and amethyst, along with veins of metasomatic crystals such as epidote, titanite and prehnite, mark the final phase of mineralising activity in the Harts Range. This probably took place at the same time as the Alice Springs Orogeny 300 million years ago (Shaw *et al.*, 1990). The sceptre-form quartz and amethyst mineralisation occurs almost exclusively within relatively small quartz- calcite veins (both minerals apparently being essential for the formation of some sceptre crystals), which transgressively cut particular bands of the Riddock Amphibolite member of the Arunta Inlier. These specific amphibolite bands have very distinctive outcrops, and may represent a metabasalt or other former lava of critical composition and with probably appreciable initial lime content. The crystal-bearing veins are most common in the near vicinity of massive pegmatites, which may have been the source of the hydrothermal mineralising fluids, which released the lime by hydrolytic alteration of the amphibolite. The best examples of the sceptre-form crystals have been collected by Aboriginal people from subsoil weathering accum-ulations, which are quite difficult to discover from the very meagre surface indications. The exact mechanisms which form these strangely distorted crystals are still a matter of conjecture, but the crystals themselves are frequently of very striking and beautiful appearance. Two mechanisms are suggested to explain differences seen in the many habits of the sceptre crystals collected. It is suggested that one be referred to as *co-crystallisation*, where the developing quartz and calcite produce the sceptre structure by regular physical distortions. The second mechanism is that of *point nucleation*, where there are two distinct phases of crystallisation, with the second initiated around the pointed apices of the initially formed crystals, which then become the stem of the sceptre structure.

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An Oxygen Isotope Thermometer for Cerussite: Applications at the Block 14 Mine, Broken Hill, New South Wales

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Slow precipitation experiments were used to determine the oxygen isotope fractionation between cerussite ($PbCO_3$) and water over the temperature range 20 to 60°C. Cerussite was synthesized at low temperatures, and analysed by methods similar to those described for malachite and azurite by Melchiorre *et al.* (1999, 2000) A 250 cm^3 glass bottle was filled with 3 g of calcite cleavage fragments, and 0.1 M $Pb(NO_3)_2$. Vessels were sealed and placed in a water equilibration bath set to the desired temperature of the experiment, and allowed to react for 8 to 12 weeks before the vesselwas removed from the bath, and the cerussite overgrowths harvested for isotopic analysis. The temperature dependent fractionation determined by these experiments is shown below,

$$1000 \ln \alpha = 2.63\ (10^6/T^2) - 3.58$$

where T is in Kelvin (Figure 1). This new geothermometer has been applied to natural cerussite samples from the Block 14 Mine, Broken Hill, New South Wales, and other localities.

To assess the reliability of this new low temperature thermometer, cerussites that have formed in historical times of known water $\delta^{18}O$ and temperature were used to independently calculate fractionation values. These very low temperature (<25°C) samples, from the Bwlch Glas Mine, Wales, United Kingdom, and the Pinnacles Mine, Broken Hill, New South Wales, plot very

Table 1. Data for the Samples

Sample Type	**Location**	**Coll. By**	**Delta 18-O** (SMOW)	**Delta 13-C** (PDB)	**Calculated Temperature** (°C)
Cerrusite	Comet Mine, Tasmania	EBM 1999	20.24	-17.78	25
Cerrusite	Brown's Deposit, Rum Jungle, NT	EBM 1997	14.58	-13.69	58
Cerrusite	Pinnacle Mine Open Cut, Broken Hill District, NSW	EBM 1999	17.58	-7.31	39
Cerrusite	Block 14, Broken Hill, 1703N, 228E	PAW 1994	16.96	-14.90	42
Cerrusite	Block 14, Broken Hill, 1760N, 172E	PAW 1994	17.32	-19.16	40
Cerrusite	Block 14, Broken Hill, 1855N, 160E	PAW 1994	17.00	-18.87	42
Cerrusite	Block 14, Broken Hill, 1990N, 175E	PAW 1994	16.71	-14.56	44
Cerrusite	Block 14, Broken Hill, 1357N, 181E	PAW 1994	16.62	-15.65	44
Cerrusite	Block 14, Broken Hill, 360N, 180E	PAW 1994	16.82	-13.85	43
Cerrusite	Block 14, Broken Hill, 390N, 200E	PAW 1994	16.20	-13.53	47
Cerrusite	Block 14, Broken Hill, NSW "first level"	EBM 1997	15.98	-17.22	48
Cerrusite	Block 14, Broken Hill, NSW "first level"	EBM 1999	16.06	-16.85	48
Cerrusite	Block 14, Broken Hill, NSW "second level"	Austr. Museum	15.82	-18.34	49

close to the trend observed for our synthetic data (Figure 2). Similarly, the high-temperature experiments of O'Neil *et al.* (1969) are also in agreement with our thermometer (Figure 2).

The $\delta^{18}O$ and δ^{13} C values of both synthetic and natural cerussites were determined by the standard method of reaction with 100 percent orthophosphoric acid (H_3PO_4) at 25°C to release CO_2 gas. The resulting CO_2 gas was purified, and then analysed on an isotope ratio mass spectrometer. The cerussite-phosphoric acid fractionation factor of 10.08 was used in the correction of data.

Oxygen isotope data for 10 cerussite samples from the Block 14 Mine, and 3 cerussites from other localities, suggest formation from meteoric waters (Table 1). Both carbon and oxygen isotope delta values for these natural cerussites are consistent with values recorded for speleothems, soil carbonates, and copper carbonates, suggesting that cerussite commonly de-

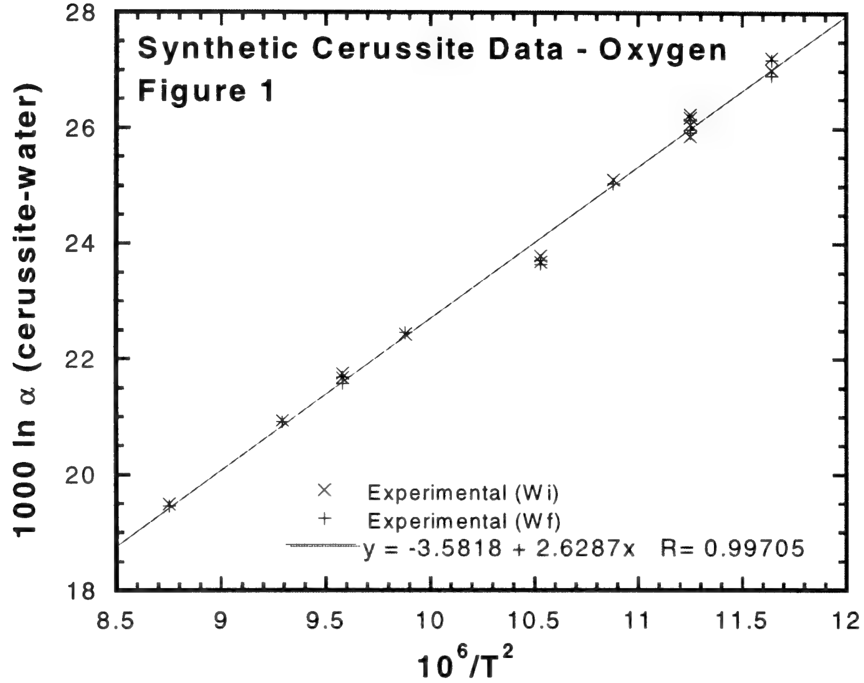

Fig. 1. Plot of experimentally derived data for the cerussite geothermometer (Wi and Wf refer to separate experimental runs).

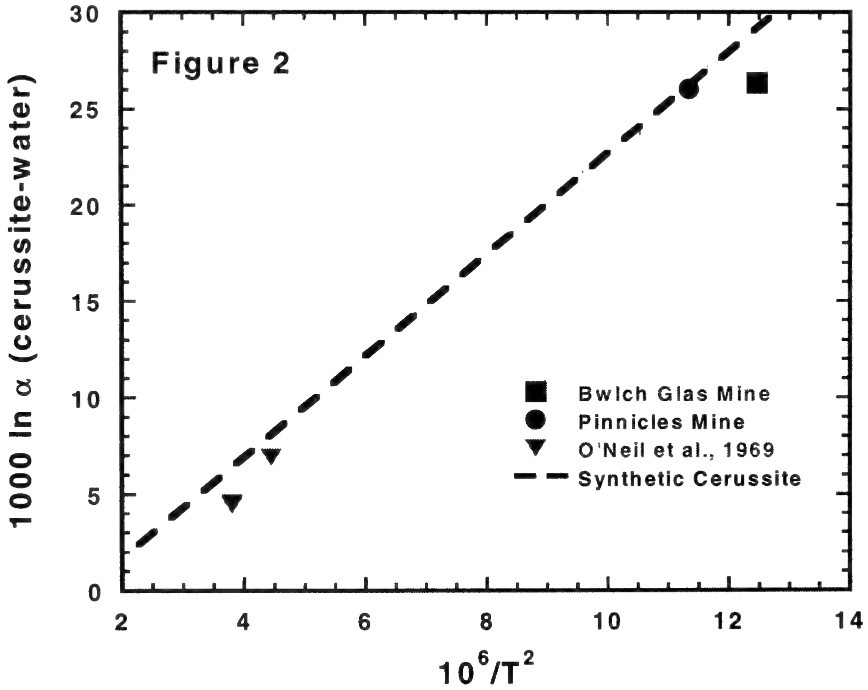

Fig. 2. Data for Bwlch Glas and Pinnacles Mines, together with the high temperature results of O'Neil *et al.* (1969). The dashed line is the experimentally determined. relationship of Figure 1.

rives much of its carbon from isotopically-light soil CO_2. Indeed, $\delta^{13}C$ values as light as -19‰ indicate a significant organic carbon source (Table 1). The new oxygen isotope thermometer indicates that natural cerussites at Block 14 formed at temperatures significantly greater than modern local air temperatures. This is consistent with malachite thermometry results at Broken Hill (Melchiorre *et al.*, 1999). We suggest that these higher apparent temperatures record the heat produced during oxidation of concentrated sulfides. Our results therefore indicate that exothermic oxidation of sulfides at Block 14 produced shallow subsurface temperatures up to at least 50°C.

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The Mineralogy of the Currently Producing Lodes, Broken Hill, New South Wales

JANE MURRAY

Broken Hill was first pegged in 1883 and within several years the extent and value of the 'Line of Lode' was realized.With an original resource of approximately 280 million tonnes averaging greater than 15% combined metal, Broken Hill is one of the greatest known mineral deposits. Now, in the second century of mining at Broken Hill, Pasminco is operating at the very extremities of the orebody in the combined underground workings of the Zinc Corporation (ZC), New Broken Hill Consolidated (NBHC) and Southern Cross mines. Despite the efficiencies of the modern mining methods, achieving the annual production target of 2.8 million tonnes becomes more challenging with every stope mined. The remaining *in situ* reserve is of significantly lower grade and more difficult to obtain than the ore for which Broken Hill is famous. Accurate geological interpretation with respect to the position of high grade ore is therefore becoming increasingly important. Mineralogy is a vital tool utilized by mine geologists to track individual lenses through the orebody.

Metal is currently sourced from the familiar Lead Lodes (2 Lens, 3 Lens) and Zinc Lodes (1 Lens, A Lode, B Lode, C Lode), but in recent years the relative contribution each lens made to production changed considerably. Marginal grade C Lode is now one of the major bulk-tonnage producing areas of the orebody. The shear zones of the Southern Cross area are being negotiated to access the sulfides of Southern A

Lode (SAL) and South Eastern A Lode (SEAL). Scattered remobilized pods of ore form the basis of the Western A Lode (WAL) stopes. Narrow blocks of A Lode and 1 Lens are being extracted from between the largely mined-out B Lode and Upper 2 Lens. Old sites of production are being revisited. Pillars of very high grade in Lower Lead Lode are being recovered from the sand-filled voids which surround them. The remnants of B Lode above its structurally-thickened, mined-out bulk are to be targetted in 2000.

The individual lenses of the Broken Hill orebody within the southern mine leases can be readily identified by the mineralogy of their ore and gangue and this classic lode individuality has been documented previously (Table 1; Johnson & Klingner, 1975; Haydon & McConachy, 1987). The essential mineralogical character of each lode is an invaluable aid to geological interpretation of the complex periphery of the orebody.

The Potosi deposit is one of only two deposits of significant (mineable) proportions discovered in the Broken Hill district. Potosi supplemented Pasminco's underground production with ore from its open pit from 1995 until its exhaustion in early 2000 (0.6 Mt mined). The Potosi orebody mineralogically and morphologically resembled Broken Hill, being comprised of discrete semi-conformable lenses of sphalerite and lesser galena associated with distinctive garnet, quartz and gahnite gangue. Some of the ore lenses were remobilized into the bounding Potosi shear zone. The study and mining of satellite Broken Hill-type deposits has become even more crucial with the depletion of the main orebody. The mineralogical character of the known Broken Hill 'hybrids' in the district provides direction for current exploration activity.

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Table 1. Gangue mineralogy of the Main Lode horizons, Broken Hill.

Ore lens	Gangue
Zinc Lodes	
A Lode	major: rhodonite, manganoan hedenbergite, quartz, garnet; minor: calcite, cummingtonite/grunerite, wollastonite
B Lode	major: quartz; minor: manganoan hedenbergite, garnet, apatite, gahnite, damourite (muscovite), rhodonite, calcite
C Lode	major: Quartz, garnet, biotite; minor: gahnite, manganoan hedenbergite, clinozoisite, feldspar
1 Lens	major: quartz, calcite; minor: wollastonite, bustamite, manganoan hedenbergite, epidote
Lead Lodes	
2 Lens	major: calcite, rhodonite; minor: bustamite, manganoan hedenbergite, fayalite-tephroite, quartz, garnet, fluorite, apatite
3 Lens	major: quartz, fluorite; minor: rhodonite, garnet

Copper Minerals from the Moonta and Wallaroo Mines, South Australia

ALLAN PRING

Moonta Mines at Moonta, Wallaroo Mines at Kadina and the smelting works at Wallaroo on the Yorke Peninsula, constitute the copper triangle of South Australia. In the 19th Century these mines were amongst the richest copper mines in the world and Moonta Mines was the first Australian mining company to pay a million pounds Sterling in dividends. The deposits of Wallaroo Mines were discovered in 1859 and those of Moonta Mines in 1861. The lodes at Moonta were fabulously rich and the profits from mining funded the development of the mines. The Wallaroo Mines required somewhat more faith and investment before they finally made a profit. Other small mines were also worked on the fields, the most important of these being the New Cornwall and Doora Mines at Kadina and the Yelta Mine at Moonta. Moonta and Wallaroo Mines were worked continuously for over 60 years, finally closing in 1923. Following the closure of the major mines at Moonta and Kadina, sporadic but unsuccessful attempts were made to re-open some of the mines on the fields. In the 1960s Western Mining Corporation and North Broken Hill Ltd intensively explored the field and found a number of additional lodes at Poona and Wheal Hughes, to the north of Moonta. These lodes were mined for copper and gold by the Moonta Mining Joint Venture between 1988 and 1993.

Detailed geological investigations of the Moonta-Wallaroo district are few, due to an almost total lack of outcrop. The principal works describing the geology and mineralogy of the mining area are Ward & Jack (1912) and Jack (1917), summarized by Crawford (1965), Parker (1990) and Pring (1988). The orebodies of the Moonta group of mines consisted of pegmatitic and quartzose veins filling fractures along faults in the feldspar porphyry. All the Moonta lodes lay within the boundaries of the Moonta Porphyry. The orebody extended over a distance of some 3 km with individual lodes to 1000 m in length. Principal ore minerals were chalcopyrite and bornite. The gangue consisted of quartz, feldspar and biotite with accessory hematite, schorl, molybdenite and fluorite. The geological setting of the Wallaroo group of mines is quite different from Moonta and this is reflected in the mineralogy of the lodes. At the Wallaroo Mines the host rocks are metamorphosed sediments, mainly biotite schists, which have been partly invaded by dykes and offshoots of the Moonta Porphyry. There were fewer individual lodes at Wallaroo Mines although they were more extended. The main lode was mined over a distance of 1000 m and to a depth of 850 m. The lodes were of a replacement-type rather than fracture filling. The mineral assemblage of the orebody consisted of chalcopyrite with pyrite and pyrrhotite; minor amounts of galena and sphalerite were also present. The gangue was quartz and carbonates; accessory minerals included schorl, apatite and scapolite. Theories of the origin and inter-relationships of the lodes at Moonta and Wallaroo are few and perhaps out-dated. Jack (1917) believed that the source of both ore bodies could be the Arthurton Granite, some 26 km south east of Moonta, and ascribed their differences in character to differences in base rock fracturing and distance from the source. Dickinson (1942) mentioned the possibility of mineral vein formation being a late phase of porphyry intrusion with the possibility that the porphyry also underlies the Wallaroo lodes. Parker (1990) provides an up-to-date review of the geological history of the field but little insight into their origins. The deposits at Moonta and Kadina are some 15 km apart and although the two deposits are hosted in different rock types the mineralization is thought to have a common history. The differences in geological setting are reflected in the mineralogies of the two deposits.

Both deposits appear to have had similar oxidized zones, which extended to a depth of between 30 and 50 m. The saline character of the ground waters in the area resulted in the formation of large masses of atacamite and this was the dominant mineral in the oxidized zones. Malachite and azurite were rare and in the lower portion of the oxidized zones, cuprite and chalcocite were the principal species. Several small pockets of uranium minerals were found at Moonta Mines associated with the amorphous organic compound thucolite. The Moonta-Wallaroo area is probably best known as a source of very fine atacamite crystals. The finest of these, over 10 cm in length, were found in the 1860s at the New Cornwall Mine, Kadina. Some early workers thought that these specimens came from Burra, South Australia, an error that was unfortunately perpetuated in parts of the literature. Moonta and Wallaroo Mines are also famous for producing exceptional specimens of cuprite, chalcopyrite, cobaltite, native copper and quartz.

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The Paragenesis and Spatial Distribution of Secondary Copper Minerals in the Eastern Mount Isa Block, Queensland

JAMES L. SHARPE

With few exceptions, the copper deposits of the Eastern Mount Isa Block are localised by faults. Economic mineralisation often occurs where faults or shears are intersected by cross-faults or tension gashes. Extensive brecciation in these locations provided the conduit for the injection of mineral-bearing fluids and the ingress of vadose groundwater bearing oxygen and ions capable of reacting with the primary sulfides to form an extensive suite of secondary copper minerals. In assessing the paragenesis and spatial distribution of secondary mineralisation it is necessary to consider not only the evidence revealed by examination of samples which may be representative of a particular part of the deposit, but also the geochemical processes that dictate the order of formation of the various species. In a natural system conditions of pH, oxidation potential, availability of reactants and naturally occurring catalysts or nucleators, *e.g.*, manganese oxides, and temperature and pressure variations all serve to create different local chemical conditions.

Native copper is found throughout the lodes but is most abundant near the water table, and historical records often refer to discoveries of native copper in the outcrop. Three distinct modes of occurrence have been noted. Throughout the shears containing the lodes and at all depths in the oxide zone it is common to find masses of highly siliceous goethite containing slugs and disseminations of native copper precipitated prior to silicification under conditions that were feebly reducing; cuprite (Cu_2O) is more likely to form with increasing Eh. At depth native copper becomes more abundant, usually as pods and stringers within cuprite and is often accompanied by nantokite (CuCl) (Sharpe and Williams, 1999). Native copper also occurs as nodules with successive cuprite, tenorite (CuO), and chrysocolla ($\sim CuSiO_3.nH_2O$) or malachite rinds.

Brochantite ($Cu_4SO_4(OH)_6$) distribution is noteworthy, the mineral being found in most deposits and at all depths, always tightly within the original lode limits. Antlerite ($Cu_3SO_4(OH)_4$) was confirmed from one deposit, the Monakoff mine. Stability relationship between antlerite and brochantite has been established showing that, compared with brochantite, antlerite forms at a higher sulfate ion activity and higher temperature ($>35^0C$). Whole or partial replacement of antlerite by brochantite is common at Monakoff. Malachite ($Cu_2CO_3(OH)_2$) is present in all outcropping deposits. On the other hand, azurite ($Cu_3(CO_3)_2(OH)_2$) is abundant in very few deposits. Stability relationships between malachite and azurite have been established showing that a partial pressure of CO_2 above $10^{-1.36}$ is required to form azurite (Williams, 1990) consistent with the observation of azurite forming only at depth.

Secondary copper phosphates are more widespread than is generally realised. Pseudomalachite ($Cu_5(PO_4)_2(OH)_4$) can be found at all the operating open cut copper mines and on most of the dumps in the Cloncurry district. Libethenite ($Cu_2PO_4(OH)$) is also widespread but is much rarer. Cornetite, ($Cu_3PO_4(OH)_3$) is relatively rare, having been found in very small quantities in only three deposits. This is in accord with stability relationships for the suite (Magalhães *et al.*, 1986). A separate, but remarkable, observation in many deposits that have been examined is the zoning of the secondary copper phosphates in the supergene profile. In particular, libethenite is always found near the top of the oxide zone but is absent at depths exceeding 10 m. On the other hand, pseudomalachite is usually quite abundant near the surface and persists to the intermediate levels of the oxide zone. Stability phase data shows that libethenite forms at most concentrated phosphate activities and pseudomalachite from solutions with lower amounts of dissolved phosphate for a given copper ion activity. Phosphate ion is released from apatite as a result of weathering and the spatial distribution of the copper phosphates may be explained by differential weathering phenomena.

During field research relatively few deposits containing copper arsenates were found. In a few, arsenopyrite or cobaltite formed part of the primary ore thus providing the opportunity for the formation of secondary copper arsenates. Conichalcite ($CaCuAsO_4(OH)$) is by far the most common copper arsenate encountered. Olivenite ($Cu_2AsO_4(OH)$) occurs sparingly, while clinoclase ($Cu_3AsO_4(OH)_3$) is rare. Whilst it could be expected that the copper arsenates would have a similar species distribution as their phosphate analogues, this is not so, particularly when much calcium ion is available as is commonly the case. The area occupied by conichalcite in the appropriate stability field increases dramatically with increasing calcium ion activity, requiring a much higher activity of copper in order preferentially to precipitate olivenite or clinoclase in preference to conichalcite (Williams, 1990).

An interesting suite of copper chlorides from the Great Australia mine has been described including the rare minerals, connellite ($Cu_{19}Cl_4SO_4(OH)_{32}.3H_2O$) and claringbullite ($Cu_8Cl_2(OH)_{14}.H_2O$), (Day and Beyer, 1995). These occur very sparingly within masses of cuprite often associated with the very rare copper nitrate, gerhardtite ($Cu_2NO_3(OH)_3$). Atacamite ($CuCl(OH)_3$) is a common associate. Chrysocolla is as common as malachite, being present in numerous deposits in the district. Most chrysocolla is found near the surface often accompanied by copper phosphates.

Examples are given of each of these assemblages and of the detailed setting in which they are found.

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Exotic Secondary Copper Mineralization in the Eastern Mt Isa Block, Northwest Queensland

JAMES L. SHARPE & PETER A. WILLIAMS

Fault-hosted mineralization in the eastern section of the Mt Isa Block, north-west Queensland, is now thought to be of hydrothermal origin, associated with the Williams and Naraku granite complexes (Wyborn, 1998). In this setting, primary metalliferous mineral suites are remarkably simple. Pyrite (FeS_2), some bearing significant amounts of Co and Ni, and chalcopyrite ($CuFeS_2$) dominate. Arsenic-rich ores comprising arsenopyrite (FeAsS), cobaltite (CoAsS), alloclasite and glaucodot ((Co,Fe)AsS), together with varying amounts of pyrrhotite ($Fe_{1-x}S$), form a less common assemblage, invariably associated with high-temperature phases such as scheelite ($CaWO_4$), wolframite ($(Fe,Mn)WO_4$) and molybdenite (MoS_2). Oxidation zones of these deposits, however, are characterized by a bewildering array of secondary phases, especially for copper species, as a result of complex groundwater anion geochemistry.

Copper sulfate, carbonate and chloride minerals are ubiquitous in the oxidized zones, with the anions being supplied by the oxidation of sulfides, dissolution of gangue minerals, or supergene capillary action. Periodic fluctuations of the water table contribute to a recharge of anions in the weathering zone. Arsenate, derived from oxidizing sulfosalts, gives rise to olivenite ($Cu_2AsO_4(OH)$), clinoclase ($Cu_3AsO_4(OH)_3$) and especially conichalcite ($CaCuAsO_4(OH)$), in notable deposits including the Lorena, Poseidon and Desolation mines. Secondary copper phosphate mineralization is extremely common throughout the Mt Isa Block (Day & Beyer, 1995; Sielecki, 1988) and complex assemblages of copper arsenate-phosphate species are known in several deposits. Their chemistries are in accord with equilibrium models developed elsewhere (Williams, 1990). Elevated phosphate activities in oxidized zones derive from intense near-surface weathering of apatite. Allied to this is pervasive secondary silicification due to the weathering of susceptible rock-forming minerals. Chrysocolla ($\sim CuSiO_3 . nH_2O$) is conspicuous in nearly all of the oxidized zones in the area.

Perhaps most intriguing is the remarkably abundant secondary copper nitrate mineralization of the Great Australia mine, Cloncurry. Large amounts of gerhardtite ($Cu_2NO_3(OH)_3$) enclosed in masses of cuprite (Cu_2O) and native copper were recovered from the B Tangye Lode, together with likasite ($Cu_3NO_3(OH)_5 . 2H_2O$) and magnificent, deep blue, acicular crystals of the connellite-buttgenbachite series ($Cu_{19}Cl_4(SO_4,NO_3)_2(OH)_{32}(H_2O,OH)_3$). In a similar setting in the Main Lode, the rare chloride mineral claringbullite ($Cu_8Cl_2(OH)_{14} . H_2O$) was fairly common, and the supposedly rare species nantokite (CuCl) was an important ore mineral (although unrecognized as such in early mining operations).

The origin of nitrate in supergene assemblages has puzzled geochemists for many decades. Suggestions for it include the leaching of nitrate-rich sedimentary strata, the formation of nitrogen oxides *via* electrical discharge during thunderstorms and photochemical processes in the atmosphere, and biological fixation of nitrogen in the soil. Stable isotope measurements of nitrate in caliche from northern Chile and California, USA, have established the probability of an atmospheric source for these deposits (Böhlke *et al.*, 1997). Very high levels of nitrate (to more than 50 ppm) in groundwaters of the Australian arid zone have been traced to bacteria in termite mounds which fix nitrogen as ammonia; this in turn is metabolized to nitrate by other organisms including cyanobacteria in the mounds and soil crusts (Barnes *et al.*, 1992). Both of the processes are likely to have played a role at Great Australia and probably still obtain. Analyses of 15 groundwater samples recovered from drill holes on the Main Lode at Great Australia, prior to the most recent phase of mining, gave nitrate concentrations of up to 11 ppm.

Finally, we note that several oxidation zones in the Block are still active. Silica-encapsulated goethite masses in the Main Lode at Great Australia, for example, contain sludges of poorly crystalline malachite/georgite ($Cu_2CO_3(OH)_2$), X-ray amorphous copper-silicate-phosphate polymers and soft, amorphous, hydrated chrysocolla-like material. This current chemical reactivity is in marked contrast to the oxidized zone of the giant Ernest Henry deposit, just north of Cloncurry, formed prior to and during Mesozoic times, and in which subsequent inundation led to the reduction of secondary copper minerals to arsenian native copper.

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The Richest Lode and the Silver City

ROBERT SOLOMON

Broken Hill and its mines are much distinguished for:

- the extent and richness of the mineral lode
- the volume and longevity of ore production
- the size and permanence of the town which the lode has supported
- the exceptional trades union influence on the life of the town
- the town's function as the centre for a uniquely extensive grazing region
- the long persistence of the mines and the settlement in a hostile environment.

MINING

Mineralogists are much taken by the wonderful variety of more than 100 minerals found in the Broken Hill lode. Lawrence (1968) wrote that for "*the variety and crystallographic perfection of its oxidised minerals the Broken Hill mining field finds a ready place as one of Nature's great museums. If the long list of primary ore minerals and gangue minerals be added, Broken Hill stands supreme in the mineral world.*" That, presumably, is why we are here.

The first Broken Hill ore produced 738 ounces of silver per ton in late 1885. It soon rose to thousands of ounces per ton, which confirmed the great value of the lode. The original syndicate of seven men must have regretted leasing their nearly 300 acres (120 ha) for five shillings per acre instead of purchasing the freehold for £2 (40 shillings), though disappointment was cushioned by the allocation in 1888 of new shares and profits to the value of £168/10/0 ($337) per share! The production of more than two million ounces (64.9 tonnes) of silver in the second half of 1888 was sufficient to establish the Hill's reputation as the world's leading silver field. It led A.C. Cooke to call his detailed 1894 drawing of the mines (reproduced in Solomon (1988)), the smelters and the town *The Australian City of Broken Hill showing the Proprietary and Principal Mines on the Richest* Silver *Lode in the World*, and for Ion Idriess to chose *The Silver City* for the title of his 1956 book (Idriess, 1956). In 1937 the gleaming "Silver City Comet" began its run between Sydney and Broken Hill.

Silver did not long continue as the mainstay of Broken Hill. The lode was described, when the Australasian Institute of Mining and Metallurgy met there in 1946, as "*a massive lead-zinc sulphide deposit forming a continuous arch...up to 300 feet in width...its...depth at the north and south ends is still unknown. The line of mineral-isation continues for at least eight miles north of the North Mine and two miles south of the Zinc Corporation workings, giving a known overall length of approximately 13 miles of mineralised belt, of which only 3.5 miles has so far been proved of economic value*" (Solomon, 1988). As you all will know, the proven ore-body runs for 7.5 km and in 1988 reached a depth of 1600 metres (just over one mile) at the north end. Before 1940, according to T.B. Dodds of North Broken Hill Ltd in 1947 (Solomon, 1988), three mining areas each produced 10-12 per cent of the world's lead: Broken Hill, whose ore contained 15 per cent lead and 12 per cent zinc; the Sullivan Mine at Kimberley, British Columbia (8.5 and 6.5 per cent); and the extensive, low-grade field of southeast Missouri (3.5 and 3.5 per cent). In the 69 years to the end of 1952, 71 million tons of ore were mined at Broken Hill, from which came 9.5 million tons of lead, 6 million tons of zinc and 572 million ounces of silver. The life of the lode was then expected to be about 50 years at the current annual extraction rate of 1.3 million tons (although proved reserves were only 15 M tons). That seems to have been a good guess, because, despite more than doubling production since the 1950s, the last mine is scheduled to close in 2006. Given the uncertainty which attended almost every stage of the mines' and town's development, its history has been quite extraordinary.

PEOPLE

The number employed to produce the impressive Broken Hill mining output grew greatly in a short time, as so often the case when valuable minerals are found. In 1887 there were about 1500 people in and on the mines. By 1890 there were 5,800 and in 1899 they passed 7,000. The peak was in 1907, when 8,820 people were employed. This was almost equalled in 1913, but World War I reduced the total to about 5,000, and the Great Depression took it down to 3,000. The post-World War II boom saw 6,000 reached again in 1953; then followed a gradual decline to the present 800 or so.

The population that supported the mining work force had a meteoric growth – from a handful in 1883 to 20,000 in 1891. This made Broken Hill the second urban centre in New South Wales, exceeded only by the State capitals in Australia. Many 19th Century mining camps around the world demonstrated this kind of growth, but more often to 10,000 than to 20,000 and few for long enough to become structured towns, let alone cities. The Hill's population graph continued to climb steeply to almost 31,000 at the 1911 Census, and then to 35,000 in 1915: most impressive for a mining settlement. The effects of war caused Broken Hill's population to plunge steeply to fewer than 27,000 at the Census of 1921. With the founding of the steel industry by Broken Hill Proprietary Ltd (BHP) in 1915, Newcastle soon pushed Broken Hill into third place among New South Wales towns, but there it stayed for almost half a century – more than 1100 km from the port city of Sydney and the New South Wales Parliament seated there. "On the edge of sundown", as Premier John Storey (in 1920) so colourfully described its location (BHP, 1920). In mid-1998 the population was down to 21,000, just above the 1891 mark, and the projection is for a little under 19,000 by 2006, when the Pasminco mine closes. The most serious aspect of the Hill's demography is the significant decrease of young people, with the under 20s falling from 38 per cent of the total in 1971 to 27 per cent in 1996. The birth rate is down and job opportunities elsewhere beckon.

MINING TOWN CULTURE

For at least its first 60 years, life at Broken Hill was tough. The climate was arduous, water was short, temperatures in uninsulated iron and timber houses were extreme (52 per cent of dwellings had walls of iron in 1933, still 34 per cent in 1954). Dust storms threatened the viability of settlement, and gave rise to the path-finding regeneration scheme. Food was basic and its variety limited. Typhoid and dust-caused lung disease were prevalent. Education was sound, with the contribution of the Technical College to the training of engineers and others well appreciated. Religion thrived, as did hard drinking and the temperance movement at one and the same time.

Union loyalty and control was the strongest known anywhere, with socialism actively embraced and the *Barrier Daily Truth* backing the workers against the bosses, but for most of the time the Barrier Industrial Council was in balance with the Mine Managers' Association, so that only three major strikes marred industrial relations on the line of lode: 1892, 1909 and 1919-20. The advent of the Lead Bonus, as a weekly wage bonus, in the 1920s did much to subdue thoughts of further strikes, for it rose from 3 shillings and sixpence in 1935 to £16/4/4½ in 1951, when the Australian Basic Wage was £12. From 1948 to 1960 the average weekly lead bonus did not fall below 75 per cent of the Basic Wage.

THE SOUTH AUSTRALIAN CONNECTION

If the mineral outcrop of "the broken hill" had been 50 km west when it attracted Charles Rasp's attention in 1883, Broken Hill's history might have been different. But, in my guess, not very. Its hundreds of millions in mining royalties would certainly have been welcomed by the South Australian economy, but trade and traffic were westward from the outset. There were 52,500 passenger border crossings in 1888 when the Silverton Tramway Co ran its first trains, and the large volume of ore was also shipped westward. By 1897 the smelters had moved to Port Adelaide and Port Pirie after a mere decade on the line of lode. The Zinc Corporation set up its holiday camp on the Adelaide seaside at Largs Bay in 1947.

Broken Hill has worked on Central Australian time for a very long time, and its STD telephone prefix is 08 while NSW's is 02. Only recently has the Hill been included in the ABC's NSW television weather summaries. Hillites have always followed Adelaide's Australian Rules competition and local stars have joined it over the years. The unions' 300-mile employment rule reinforced established connections by admitting Adelaideians and excluding Sydneysiders. There's no evidence that the city of churches influenced Broken Hill's Methodists to become even more temperate than they were, whereas the annual mid-summer Burra-Broken Hill barrow race undoubtedly created a great opening for West End beer.

THE REGION AND THE FUTURE

While Broken Hill's lifetime role of service centre to a vast agricultural region can be predicted to continue indefinitely, that is limited by the small population carrying on extremely low density grazing and by the bottom recently falling out of the always-reliable Australian wool market. The somewhat unexpected development of arable agriculture on Lake Tandou in the Menindee Lakes system in the late 1980s was a real morale-booster, but one which water availability will not allow to be substantially increased. So, it is to tourism that Broken Hill seems likely to link its future welfare (as I wrote (Solomon, 1988) in the final chapter of *The Richest Lode* in 1988). Who, in 1891 or 1920, would have imagined Broken Hill's mining base being replaced by tourism? But in those distant days the prospect was of mining's replacement by nothing, and much sooner than 120 years after it so strikingly began. And who would have thought, with the residents reduced to little more than half their 1915 peak, that their standard of urban amenity would be undreamed of by the pre-pipeline miners and townspeople?

Who would have imagined, in 1891, or in 1920, Broken Hill's mining base being replaced by tourism?

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Mount Isa: a Mineral Deposit of World Significance

GEORGE STACEY

Mount Isa in northwest Queensland is recognised as one of the world's great mines. Since its discovery in 1923, Mount Isa has produced over five million tonnes of copper, 21 million kilograms of silver, five million tonnes of lead, and five million tonnes of zinc. Silver and lead production is second only to Broken Hill and substantial reserves of copper and silver lead and zinc ores remain; large scale mining and processing operations will continue well in to the 21st century.

Mount Isa was discovered by a lone prospector, John Campbell Miles, in 1923 and Mount Isa Mines Limited was formed as a company in 1924 (Blainey, 1960). Mining and smelting of the oxidized lead ores, containing almost exclusively cerussite, began in 1931. It was not until 1935, when mining of primary sulfide ore began, that the first zinc concentrates were produced. During the 1930s the existence of copper ores was confirmed and in 1943 the mine ceased silver-lead-zinc production and switched to copper to help the war effort. Copper mining ceased from 1946 to 1953, then production from the copper orebodies began. Current underground ore production is approximately 32,000 tonnes per day, making it one of the largest underground mines in the world.

The silver-lead-zinc deposits at Mount Isa run in a northerly direction and occur in a sedimentary formation up to 1000 metres thick, the 1600 Ma Urquhart Shale. This consists of alternating sedimentary beds with carbonaceous siltstone rich in fine-grained pyrite and pyrrhotite. The parallel bedded silver-lead-zinc orebodies occur in close proximity to, but are geologically and spatially quite distinct from, breccia hosted massive to disseminated copper mineralisation. Virtually no copper occurs in the silver-lead-zinc orebodies and no lead-zinc in the copper orebodies. Some 20 km north of the Mount Isa mine, the silver-lead-zinc orebodies of the Hilton Mine are also restricted to the Urquhart shale and closely resemble the primary ores of the Mt Isa mine. The only primary copper mineral at Mount Isa is chalcopyrite associated with pyrite and pyrrhotite as disseminations and vein fillings situated within zones of brecciated and recrystallized Urquhart Shale known as "silica dolomite." The earliest discovered copper ore was that of the 650 Orebody. The deeper and larger 1100 Orebody at the south end of the mine was first intersected in the early 1950s (Sielecki, 1988).

Good specimens of oxidized lead minerals are relatively rare at Mount Isa. The only oxidized lead minerals of major significance to the collector are the fine specimens of *camphyllite* (arsenian pyromorphite) found near the surface in the vicinity of the Lawler Shaft and in the Black Star Open Cut during early mining operations. These are equal in quality to the best *camphyllite* found anywhere and occur as classically barrel-shaped crystals up to 10 mm in size, ranging in colour from bright lustrous orange red crystals of world class to yellow, caramel and greenish-yellow to green. The best crystals occur in association with surface clays and shales and fine specimens, over 30 cm long covered with large, lustrous semi-botryoidal crystals, were recovered in the early days.

The Black Star Open Cut, situated in the oxidized zone of the silver-lead-zinc orebodies, commenced operation in the 1930s. Since that time it has been mined intermittently as a source of siliceous flux for the lead smelter. In the early days a number of specimens were recovered from this source showing classic barrel shaped crystals of *camphyllite*. Since the second world war the deposit has been primarily noted for its attractive specimens of silicified shale displaying sharp, freestanding hexagonal prisms of yellow pyromorphite crystals. Individual crystals of pyromorphite range up to 5 mm across and 25 mm long. The Black Star Open Cut.is also noted for vughy limonite containing pure white, lustrous cerussite in fine dendritic sixlings up to 3 cm across, displaying reticulated twinning. Occasionally some prismatic crystals of opaque white anglesite to 5 mm in length have also been found. Very little zinc occurs in the oxidized zone but on occasions, smithsonite of fairly poor quality has been recovered; one small pocket of pink smithsonite, due to the presence of cobalt, was found in the late 1960s.

In 1957 production of copper at Mount Isa recommenced with the discovery of the Black Rock Orebody, which was found just underneath the surface about 500 metres south west of the old mine office. The deposit contained large quantities of secondary copper minerals and consisted of an oxidized sequence of Kennedy siltstone and shale resting upon Urquhart shale, which had been partly oxidized and kaolinized to variable depths. Open cut operations ended in 1965 with a pit some 165 metres deep. The Black Rock Open Cut was in the oxidized zone of the 500 Copper Orebody. The deposit contained no lead or zinc minerals.This deposit, when mined during the 1960s, produced some outstanding specimens of native copper, large gem-like cuprite crystals to 2 cm, red lustrous *chalcotrichite*, and chrysocolla often in association with tenorite, cuprite, and native copper. The Black Rock Open Cut produced some outstanding spinel twin crystals of native copper coated with a thin protective film of cuprite. Many of these crystals were from 4 to 10 cm in size with some specimens made up of superb crystal groups containing from 3 to 6 large crystals. A small number of notable specimens of native copper, some with lustrous transparent pale amber coloured barite crystals in association with skeletal silica were recovered from the upper levels of the 500 Orebody where drives on 4 level were used to access a ventilation shaft. Some good specimens of native copper crystals and crystals of calcite and barite were also recovered from cavities adjacent to fault zones and occasional vughs underground in the copper mining areas.

Over a 100 different mineral species have been reported from the Mount Isa mine but most of these are of minor or insignificant occurrence. During its operation Mount Isa produced only a few mineral species of significance on the world scene and, unfortunately, very few of these survive today.

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Geodiverse Gemstone Deposits, New England, New South Wales

F. LIN SUTHERLAND

The New England terrain provides a cornucopia of gemstones, an inheritance from a fold belt of Palaeozoic rocks, disrupted by granitic emplacement and veneered by volcanic and sedimentary deposits. This gemstone diversity (Webb and Sutherland, 1998) stems from three main rock associations. Continental volcanics supplied diamond, sapphire, ruby, zircon, garnet, feldspar, olivine and precious opal. Many gemstones were weathered out and flushed into alluvial deposits. Some did not form in their molten hosts, but rose up in melts that broke through metamorphic assemblages. Granitic bodies, veins and contacts supply topaz, beryl (including emerald), quartz, garnet and ruby-amber cassiterite. Again many crystals are reworked into abraded stones. The metamorphic fold belt supplies rhodonite, nephrite jade and a variety of cherts, jaspers and agates. These largely provide polished ornamental stones. New England began diamond mining in 1872 and in 2000 the Copeton and Bingara fields remain under exploration. The diamonds prevail in Cainozoic sub-basaltic deposits and their origin is problematic. Crystals show strong 'magmatic' resorption and are unusual, being made of heavy carbon and containing unusual inclusions (coesite, calcium-rich silicates) which yield 'young' formation ages. White (low nitrogen) and yellow (high nitrogen) diamonds are found. Their source remains controversial, whether derived from underlying diamond-bearing seafloor slabs (Barron *et al.*, 1996) or transported from afar (Davies *et al.*, 1999).

The Inverell-Glen Innes gemfield is a principal supplier of sapphires. Most stones are blue, green or yellow and often colour zoned. They are mostly shed from volcaniclastic deposits, but initial parentage is controversial, perhaps having formed from mid-crust interactions of carbonatitic and silicic magmas (Guo *et al.*,

1996) or from deeper feldspathic melts (Sutherland *et al.*, 1998a). Some fields yield 'fancy coloured' sapphires, grading into ruby (Sutherland *et al.*, 1998b). Zircon, an abundant associate of sapphire, adopts many crystal habits and colours. It is cut as a minor gemstone. Crystals range from pale, anhedral, lower-U types to more euhedral, darker coloured higher-U types. Radiometric dating indicates an origin closely, but not directly, related to basaltic volcanism (Sutherland *et al.*, 1993).

Beryls including emerald were mined from 1890. Yellow, green to blue and deeper coloured aquamarine and emerald varieties have been cut. The main material comes from pegmatite veins around the Mole Granite near Emmaville-Torrington (Brown, 1984). Recent finds of strongly banded beryl/emerald provide unusual cut stones. High grade gem quality topaz is widespread in granitic lodes and alluvial distributions (Smith, 1926). Large, limpid, colourless, green, yellow and blue crystals, some with pink brown tinges, provide flawless cut stones.

Abundant quartz varieties come from granitic bodies and related siliceous pipes. They include rock crystal, smoky quartz, brown quartz, amethyst, citrine, cairngorm, morion, rare rose quartz, as well as rutiled quartz, sceptre quartz and aventurine. Optically perfect quartz was mined from Kingsgate pipes. Deposits in foldbelt serpentinites southeast of Tamworth have produced export quality jade. It forms as bluish green to dark green lenses and the less sheared material takes a good polish. Lapidary grade rhodonite comes from manganese deposits within southern foldbelt sequences. Brownish to deep red and rose pink material has been mined. These old sea floor deposits became enhanced in colour by thermal effects near granite contracts. Pyrope-almandine garnets of gem quality are found in sporadic basalt associations. Faceting-quality peridot (olivine) and feldspar (labradorite) are found in rare basalt flows, while some precious 'volcanic' opal occurs in basalt and rhyolite lavas in northeastern areas. Green fluorite and ruby-amber cassiterite provide collectors gemstones from granitic deposits. A wide range of lapidary cherts, jaspers and agate pebbles can be fossicked in the fold belt drainages.

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Argyle Diamond Deposit, Western Australia

GAYLE WEBB

Argyle burst onto the world scene in the early 1980s and has since changed many aspects of diamond exploration and marketing. It is the largest diamond mine in the world, the largest producer of natural industrial diamonds and a significant producer of gem quality diamonds. The mine is in the East Kimberley region, about 2,400 km north-east of Perth, and is virtually one huge pipe with associated alluvial deposits. The Ashton Joint Venture identified diamonds at Smoke Creek in August 1979. Following the stream to its source, 20 kilometres away, geologists discovered the Argyle Pipe in October 1979. Named after nearby Lake Argyle the pipe was referred to as AK1. This pipe subsequently provided extremely rich diamond grades of 7 carats per tonne, 10 times higher than any known deposit. Argyle has proved unique in a number of areas: geological, mineralogical, and commercial.

The geology of the Argyle Pipe did not fit the existing model for diamond exploration and the normal suite of kimberlitic indicator minerals was absent. The main indicator proved to be diamond itself, with some chromite. Previously, kimberlite intrusions in old continental cratons, stable for billions of years, had been considered the primary source of terrestrial diamond. At Argyle, diamonds were found for the first time in an adjoining mobile zone. A further deviation from the accepted model was the olivine-rich lamproite in which the diamonds occurred. This was a new diamond-bearing rock and widened the range of potential diamond hosts. The Argyle Pipe is an olivine lamproite diatreme of Precambrian age with a surface area of 50 hectares. It is an elongated body, 2 km long, that varies in width from 500 m to 150 m. The pipe has been faulted and tilted before erosion. At depth, the diatreme is variable in shape. Like most diamonds, lamproitic diamonds are mantle xenocrysts transported and resorbed by their volcanic host. They come from depths of over 180 km in highly-explosive, rapidly-injected magmas. Diamond emplacement in the larger Kimberley region was sporadic, from Precambrian into Tertiary time (2000 to 20 Ma), but the Proterozoic Argyle pipe (1180 Ma) carried the only economic concentration of diamonds.

The Argyle Joint Venture estimated that the mine would supply more than 25% of the world's diamonds over 20 years. A two-stage mining program was formulated. Stage 1 began in 1983, with the short-term mining of alluvial deposits at Smoke and Limestone Creeks and scree overlying the AK1 pipe. From 1983–1985, 16.8 million carats of diamonds were produced. Stage 2 began in 1986 with the long-term mining of the main orebody. Production jumped to 29.2 million carats. Production reached over 30 million carats annually, about one third of the world's rough diamonds. In 1993, due to expansion and upgrading, a record 40.9 million carats was produced. Figures are still high, with 40.2 million carats produced in 1998.

In spite of its huge production figures, only about 5% of Argyle's total output is gem quality. The vast remainder is about 50% industrial grade and 45% cheap, near-gem quality. The quality of the alluvial diamonds is reputedly higher, with 10% being gem quality. This low gem ratio reduces the output to only 5 per cent, by value, of the world's gem quality diamonds, yet this small percentage generates 50% of the mine's revenue.

The majority of Argyle diamonds (95%) are eclogitic in type. They are dodecahedral or mixed crystal forms and are 1.2 to 1.6 billion years old, formed shortly before eruption. However, peridotitic, octahedral crystals also occur and these have a formation age of 3 billion years. Argyle diamonds provide many contrasts with African and Russian stones. They are typically small, averaging 0.10 carats. To date, the largest stones found have been between 40 and 50 carats. They are characteristically irregular in shape, with heavily etched surfaces attributed to their transport in corrosive potassic melts. Unusual hexagonal etch pits and trigons with truncated corners contrast with the sharply triangular etch features on many African crystals. The colour distribution of gem quality diamonds from the Argyle Mine is unique. They are dominantly brown, with less than 20 % being colourless or yellow shades. Less than 0.001% of total production is pink to red. Occasionally, blue and green stones are found. The pink and brown colours are due to plastic deformation of the crystal lattice. Argyle blue stones are unusual in being coloured by hydrogen, rather than a boron impurity. Argyle provides the world's only reliable supply of rare pink diamonds. A grading system was devised for these stones, which could include a range of colours from purplish pink to mixed shades, like *pink champagne*. Since 1984, Argyle Diamond Sales has held an annual Pink Diamond Tender in Geneva to sell its outstanding pink to red stones. Such stones have sold for $1,000,000 per carat.

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Mine Geology and Mineral Localities at Broken Hill, New South Wales

TONY WEBSTER

Many of Australia's great ore deposits have produced mineral specimens of exceptional quality with the Palaeo- proterozoic Broken Hill lead-zinc-silver deposit in far western New South Wales being pre-eminent. At Broken Hill, the compositional complexity of the various orebodies, coupled with high grade regional metamorphism and the subsequent exposure of the orebodies to near-surface weathering processes has produced an exceptional variety of minerals.

The first recorded specimen from Broken Hill was collected by Charles Rasp in 1883. It was a heavy black material that contained minor silver and lead and was probably coronadite. The outcrop, from which it came, was a distinctive linear ragged hill, the "broken hill" which is often referred to as a gossan, but true gossan only becomes a significant proportion of the oxidized zone at depth. At Broken Hill, the oxidized ore types are all closely associated with a plunge culminating in the centre of the field. It is only here that the mineralisation was close enough to the surface to have been affected by surface oxidation. The geology of the upper Broken Hill Proprietary mine shows that most near-surface mineralisation was 3 Lens lying in the hinge of an antiform.This fold hinge only reached the surface over a maximum strike length of approximately 720 metres in MLs 12 and 13 and was just being exposed at the crest by erosion when mining commenced. Distribution of the minerals was not random in the oxidized zone since mineralogically distinct regions existed. Though opinions of various workers differ on the zones that they define, Jaquet (1894) recognised the following mineralogical zones: *manganiferous iron ore* formed the surface capping; *dry high grade ore* was "*chiefly kaolin with some garnets and quartz 30 oz to 300 oz Ag/ton, 5% Pb;*" *carbonate of lead ore* was "*a loose aggregation of crystals of cerussite and a quartzo-aluminous gangue impregnated with manganiferous iron oxide. 5 oz - 80 oz Ag/ton, 20 - 60% Pb/ton;*" *dry low grade ore* differed from carbonate of lead ore in containing a much smaller percentage of cerussite; it consisted of a mixture of carbonate of lead ore and dry high grade ore; *sulphide ore*.

Mine geology shows that the geometry of the oxidized zone and outcrop was controlled by the shape of the underlying garnetiferous lode rocks and mineralisation. The richest ore type of the oxidized zone was the kaolin-dominated mineralisation which Jaquet (1894) named "*dry high grade ore*" (*i.e.*, silver-rich). It was best developed in three southerly plunging shoots at the boundary of MLs 11 and 10. The southerly plunge of the shoots suggests that there was some geological control on its formation, other than the water table. Kaolin, the main constituent, would not be the product of the breakdown of sulfides and it is probable that this ore type formed within leached metasediments. Silver-rich solutions originating from the weathering of sulfides may have been channelled down the synformal keel with silver deposited as bromian chlorargyrite in the clay. A number of.large vughs ranging from 4.5 x 1.8 x 1.8 metres to 2.7 x 4.5 x 12 metres, was developed in the heart of the ironstone body, probably the equivalent of the oxidation collapse zone, in ML 11. Some vughs were spectacular sights, with smithsonite covering black stalactites of coronadite and carpeting the floor of the cavity. A silver-rich zone of supergene ore was developed between the sulfide and oxidized ores, up to 1 metre in thickness, composed mainly of secondary silver sulfides and large blocks of native copper.

The sulfide zone is dominated by sphalerite and galena, together with gangue minerals defining distinct layers and zones. The earliest minerals are the sulfides, pyroxenes, pyroxenoids and calcite. Some parts of the orebodies were subjected to slightly higher temperatures and pressures than others, and hence the northern end of the deposit was noted for the quality and abundance of rhodonite. The best rhodonite specimens were found in 3 Lens in the North Mine, because the temperature at the time of main deformation was slightly higher than in other regions of the deposit. Bustamite was best developed within calcite-rich parts of 2 Lens, within high grade shears zones, and was encountered in stopes between the 18 and 20 levels of the Zinc Corporation Mine (ZC). In 2 Lens, most of the rare specimens of fayalite and ilvaite occurred at the margins of large masses of rhodonite where it was in contact with banded calcite ore.This was especially the case between the 19 and 21 levels at the New Broken Hill Consolidated Mine (NBHC). Green feldspars are associated with large bodies of pegmatite that traversed the lode, or formed in small melt segments in adjoining metasedimentary wall rocks.

Many minerals specimens were found lining vughs and cavities associated with well-defined fault zones in the ore. The Central and Flat Faults at the ZC and NBHC Mines were major sources of inesite, manganoan calcite, rhodocrosite, sturtite and "dogstooth" calcite. Bannisterite and gem rhodonite were recovered from fractures that were possibly associated with the Central Fault on the 12 level at the ZC Mine. Lords Hill Fault was a source of these minerals in the North Mine. "Hairy" bustamite was discovered in faults and fractures in both the North Mine and the ZC-NBHC Mines. Such environments are very unusual places for pyroxenes and pyroxenoids to crystallize. Dyscrasite in the Australian Broken Hill Consols lode developed where a geologically late fault crossed an amphibolite layer adjacent to the main orebody. Similar veins were identified in the Browne Shaft workings (12 level). Even later were the brecciated fault zones that fractured and milled the ores but were then cemented and lined with pyrite, calcite and manganoan calcite.

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The Foundation of the Sydney School of Coordination Chemistry

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ABSTRACT. The so-called 'Sydney School of Coordination Chemistry' has had an immense, even definitive, influence on Australian inorganic chemistry. Australian coordination chemists have been at the forefront of developments in the area and the international influence of many of the key figures (eg. Dwyer and Nyholm) has been widely acknowledged.

The founders of the 'School' were E.E. Turner, an Englishman who briefly held an appointment at the University of Sydney (1919-1921) and George Joseph Burrows, who after Turner's return to England influenced colleagues and research students toward careers in coordination chemistry. The scientific backgrounds of the founders and the state of inorganic chemistry at the time of foundation have been considered in detail. World War I significantly changed university education and the attitude of governments to scientific research. The timing of these influences ensured that the new foundation would become firmly established.

INTRODUCTION

It is generally agreed that the first research in coordination chemistry in Australia was carried out at the University of Melbourne (Baker & Livingstone, 1985; Mellor, 1976). The legendary professor of chemistry, David Orme Masson and Bertram Dillon Steele, later to be professor of chemistry at the University of Queensland, demonstrated that copper was present as a cupritartrate anion in Fehling's solution (Masson & Steele, 1899). This work was revisited by Packer and Wark at Masson's suggestion some twenty years later (Packer & Wark, 1921). After this initial foray Masson did no further work in coordination chemistry (Weickhardt, 1989) and Steele also did no further work in this area, concentrating his energies on the development of a unique design of microbalance (Hardman-Knight, no date; Chiswell, 1986).

The leadership in coordination chemistry in Australia passed to the University of Sydney in the late 1910s and a 'school', as it is generally understood, was founded that was extremely influential in defining inorganic chemistry in this country, as well as having a significant impact on world chemistry. This school is often referred to as the Sydney School of Coordination Chemistry (Craig, 1987).

BACKGROUND TO FOUNDATION

Coordination chemistry was a relatively young and active field of chemistry in the 1910s. The development of the field had occurred mainly through the efforts of Alfred Werner in Zürich. In his work Werner contributed significantly to the understanding of valency through introducing the concept of auxiliary valencies (German: *Nebenvalenzen*) to explain the binding in coordination compounds (Werner, 1911a, p.57):

> 1. Principal valencies are manifestations of affinity, which permit their saturation capacities to be measured in terms of hydrogen atoms or groups equivalent to the latter.

2. Auxiliary valencies are manifestations of affinity which bring about stable union of radicles; the latter being able themselves to exist as independent molecules.

Werner went on to point out that for sodium nitroprusside it is practically impossible to decide to which class of valency the NO groups belongs. Having explained that the bonding can be represented similarly for both types of valency, he continued "Nevertheless, it appears desirable to preserve for the present the difference between principal and auxiliary valencies, for to-day the doctrine of valency is in a transition state, and hence it is judicious to construct sharply defined conceptions....." (Werner, 1911a, p.66). Werner's ideas were first published in the 1890s but it was only on the publication of his book *Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie* in 1905 that significant attention was paid to his ideas. This work went through five editions in German [1905, 1909, 1913, 1920 (edited by P. Karrer) and 1923 (edited by P. Pfeiffer)] (Kauffman, 1966, p. 120). The second edition was translated into English (Werner, 1911a) with the title 'New Ideas on Inorganic Chemistry' by Edgar Percy Hedley, a Lecturer in Chemistry at the University of Birmingham. It is noted on the title page that the work is "translated, with the author's sanction, from the second German edition". This publication must have significantly assisted in bringing Werner's work to the attention of English-speaking scientists.

Werner was able to determine the structure of six-coordinate complexes by considering what isomers were possible for various combinations of ligands. This approach was an extension of the reasoning by Van't Hoff and Le Bel that led to the proposal of the tetrahedral arrangement of bonds for carbon (Jaques, 1993).

For six-coordinate complexes, four structures were considered possible: (i) hexagonal pyramidal, in which the metal atom sits above the plane of the six donor atoms which are arranged in a regular hexagon; (ii) hexagonal planar, in which the metal atom sits at the centre of a regular hexagon defined by the donor atoms; (iii) trigonal prismatic, in which the metal atom is at the centre of a trigonal prism defined by the donor atoms; and (iv) octahedral, with the metal atom sitting at the centre of a regular octahedron defined by the donor atoms. The first structure, hexagonal pyramidal, can be considered a special case of hexagonal planar (or *vice versa*) so only three structures need be considered.

For systems with only monodentate ligands only one isomer is possible for each of MA_6 and MA_5B for all structures. For MA_4B_2, the hexagonal planar and trigonal prismatic configurations would each result in three possible geometric isomers, whereas the octahedral configuration would result in only two possible geometric isomers (*cis* and *trans*). Again, for MA_3B_3, the octahedral configuration would yield two geometric isomers whereas for the other configurations three isomers would exist. Werner directed synthetic efforts at complexes of these formulae (MA_4B_2 and MA_3B_3) and other complexes containing bidentate ligands. His results strongly support the octahedral configuration but it was realised that failure to produce a third isomer was negative evidence and may have only reflected the inability to achieve the synthesis. Werner recognised that the resolution of optical isomers would confirm the octahedral configuration.

Werner wrote to his friend and fellow student Arturo Miolati on 20 February 1897 explaining that they were engaged in attempts to resolve cobalt complexes and in a paper published in 1899 on oxalatobis(ethylenediamine)cobalt(III) salts Werner discussed the possibility of the formation of asymmetric isomers, which he carefully distinguished from the optical isomerism displayed by carbon compounds in which one carbon atom has four different groups attached (Kauffman, 1981, p.122). Werner realised that complexes containing bidentate ligands would, for certain stoichiometries, yield resolvable optical isomers. Victor L. King spent a year trying unsuccessfully to resolve $[Co(en)_2CO_3]Br$ (en = ethylenediamine) and reasoned that working on a related compound $[Co(en)_2(NH_3)Cl]Cl_2$ might be more successful (Kauffman, 1981, p.125). The successful resolution was eventually achieved in June 1911 and the paper was dispatched that month for publication (Werner, 1911b). In what now would be considered an unusual convention, Werner was the sole author of the critical paper but at the head of the experimental section was "(Von V. L. King)". Werner's assistant, E. Scholze, was also acknowledged for collaboration on this paper (Werner, 1911b). Werner summarised (Werner, 1911b, translated in Kauffman, 1968, p.163) the importance of the results of this work as follows:

> (1) the proof that metal atoms can act as central atoms of stable, asymmetrically constructed molecules and thereby lead to phenomena which agree with those produced by the asymmetric carbon atom; (2) the proof that pure molecular compounds can also occur as stable mirror-image isomers, whereby the difference between valence compounds and molecular compounds, which is still frequently maintained, disappears entirely, and (3) the confirmation of one of the most far-reaching conclusions from the octahedral formula, by which the latter has found a new, important confirmation.

Subsequent to this important work, Werner was able to resolve further optical isomers of various complexes. The complexes contained ligands that included carbon atoms and it has been surmised that detractors suggested that the optical activity arose from asymmetric carbon atoms (Kauffman, 1966, p.37). Werner resolved the optical isomers of the carbon-free complex ion tris[tetrammine-μ-dihydroxocobalt(III)]cobalt(III), isolated as the bromide: $[Co\{(\mu\text{-}OH)_2Co(NH_3)_4\}_3]Br_6$, which dispelled these doubts (Werner, 1914). This remarkable achievement of a completely carbon free optically-active octahedral complex has only been repeated on a few occasions since (Kauffman, 1981, p.134).

Werner was awarded the Nobel Prize for Chemistry in 1913. In the presentation speech, Nordström, the President of the Royal Swedish Academy of Sciences stated (Nordström, 1913):

> By far the greatest interest in the field attaches also to the discovery he made in the last few years, that certain cobalt, chromium, iron and radium compounds with an asymmetrical metal atom in the complex radical can de divided into two forms which behave like mirror images and show differences of the same kind as those in organic mirror-image isomers, i.e. they are optical antipodes of each other. This discovery is a splendid support for Werner's theory. It has been called the most important discovery in chemistry in recent times, and his stereochemical work makes him the founder of inorganic stereochemistry.

Read, who completed his doctorate with Werner at Zürich (1907) and subsequently was Professor of Organic Chemistry at the University of Sydney (1916-1923), remarked later that the resolution of the salts of $[Co(en)_2(NH_3)Cl]^{2+}$ into optically active isomers "was a stereochemical achievement of the first order, confirming the octahedral environment of the central metallic atom" (Read, 1947, p.264).

Optical isomerism thus had a central role in the establishment of the structure of coordination compounds and the resolution of optical isomers of octahedral complexes has been a continuing theme in the history of coordination chemistry.

FOUNDATION

Credit for the founding of the Sydney School must go to Eustace Ebenezer Turner (1893-1966), who briefly held an appointment as lecturer at the University of Sydney from 1919-1921. Though Turner's time in Sydney was short, his influence was immense, particularly on George Joseph Burrows (1888-1950). It is through Burrows that the Sydney School was established.

Turner studied chemistry at East London College (now Queen Mary College), supported by an exhibition from the Drapers' Company, graduating B.Sc. in 1913 with first-class honours in chemistry. He found the professor of chemistry, J.T. Hewitt, a stimulating teacher who presented all areas of chemistry as equally interesting. After his B.Sc. Turner stayed one year at East London College, where he started a course on practical physical chemistry. In 1914 he was appointed as an Assistant Lecturer in Goldsmiths' College but spent most of World War I in war work. He worked on medicinals at Boots' Laboratories, Nottingham and Huddersfield Technical College for a few months at each location. Subsequently he worked on arsenicals as assistant to W.J. Pope at Cambridge. Interestingly, he published several papers in this period, including preliminary work on the structure of the biphenyls, an area in which he subsequently made a substantial contribution (Ingold, 1968).

Prior to his appointment at the University of Sydney, Turner had made some contribution to inorganic chemistry. His first publication (Bennett & Turner, 1914) opens with the statement: "The object of this investigation was to obtain organo-metallic derivatives of chromium." Anhydrous chromium(III) chloride was reacted with "the Grignard reagent" (phenyl magnesium bromide). The expectation was that $Cr(C_6H_5)_3$ (or perhaps $CrCl(C_6H_5)_2$ or even $CrCl_2(C_6H_5)$) would be obtained. The reaction was found to yield diphenyl ($C_6H_5{\cdot}C_6H_5$). The reaction was extended using other Grignard reagents to prepare α,α-dinaphthyl, dibenzyl and 4,4'-dimethyldiphenyl. Attempts to obtain asymmetric products (eg 4-methylphenyl-α-naphthalene) and products from aliphatic halides were not successful. Turner subsequently showed that copper(II) chloride could also be used as a coupling reagent, giving diphenyl from phenyl magnesium bromide (Krizewsky & Turner, 1919) and yielding 2,2'-dimethyldiphenyl from the appropriate Grignard reagent (Turner, 1920). It is to be noted that Turner's interest in the structure of diphenyl and related compounds was one of the principal lines of research that he pursued for many years. R.J.W. Le Fèvre worked with Turner at East London College in the 1920s and they co-authored eleven papers on the structures of diphenyl in 1926-8. It can be argued that Turner exerted an immense influence on chemistry at the University of Sydney, directly through his own time there (1919-1921) and indirectly through his student being appointed to a chair there from 1946-1970.

Turner's work on Grignard reagents and their reactions with transition metal compounds was only tangentially related to inorganic chemistry and was more in the sphere of organometallic chemistry rather than coordination chemistry. From his war work with Pope, he gained great experience in arsenic chemistry (Pope & Turner, 1920). In the paper it is acknowledged that "permission for its publication has been given by the General Staff."

Turner had made a strong contribution to the understanding of the structure of coordination compounds by a vigorous defence of Werner's theories. John Albert Newton

Friend published a series of papers (Friend, 1908a, 1908b & 1916) in which he proposed a cyclic theory for the structure of complexes. Friend was concerned that the "dissociable chlorine atoms hover in an indefinite manner" around the complex ion as a whole. He was also concerned that the valency (of six) proposed for cobalt was too high (Friend, 1916). Friend suggested that the chloride ions were attached directly to the cobalt atom thus exhibiting a valency of three and that the other groups were bound together in a hexagonal planar arrangement of donor atoms (in $[Co(NH_3)_6]Cl_3$, nitrogen would display a valency of five because it was bound to three hydrogen atoms and two adjacent nitrogen atoms). In his terms, "the cobalt atom lies in the ring from which it cannot easily escape for purely physical reasons". In the case of $[Co(NH_3)_5Cl]Cl_2$, one of the chlorine atoms would be in the ring, as well as bound to the cobalt, and the other two would be bound directly linked to the cobalt atom.

In his response to Friend's proposals, Turner demonstrated an understanding of the importance of optical isomerism in establishing the octahedral structure of six-coordinate complexes (Turner, 1916):

> The strong point of Werner's theory is the definite proof that the six-coordinated atoms or groups have a more or less well-defined octahedral orientation. Unless Friend's "shell" is identical with Werner's octahedral structure, there is no explanation on the cyclic theory of the existence of optical activity among certain types of compounds.

Clearly, Friend's proposal had, as an essential element, a tendency of nitrogen compounds to form ring structures. He suggested that the ammonia molecules can combine in the same way as "atmospheres" of water molecules surrounding ions as had been proposed by Kohlrausch to explain ion mobility in solutions (Friend, 1916). In modern terms, the formation of such "atmospheres" would depend on hydrogen bonding rather than a direct O-O bond as Friend claimed. Turner dismissed Friend's suggestion by reference to current understandings of nitrogen chemistry (Turner, 1916):

> Friend refers to the analogy between metalammines and ring compounds of carbon, but he seems to overlook the fact that unless some strong salt-forming influence is at work, nitrogen atoms do not combine together in the way that is so characteristic of carbon.

In the 1910s, Turner, coming from the synthetic tradition, had worked with Grignard reagents, in an attempt to prepare organometallic compounds, had gained experience in the chemistry of arsenic compounds and also had acquired a significant appreciation of the current theories of coordination compounds.

At the University of Sydney, he had the opportunity for sustained research. The work that he chose to do reflected his background and experience in that he worked on compounds of fundamental importance to the debate on bonding in coordination compounds and pursued further work on arsenic compounds. In this work on the constitution of coordination compounds and new organic arsenicals, Turner collaborated with Burrows. One of their principal triumphs was to demonstrate optical activity in an arsonium salt even though the racemisation was extremely rapid. The cation isolated was the phenyl-α-naphthylbenzylmethylarsonium ion, ie with an arsenic atom bound to four different groups. They also were able to clarify a controversy over the correct formulation of the nitroprussides by conductivity and cryoscopic measurements.

Turner returned to England to take up a research appointment at the Royal Arsenal, Woolwich and re-joined East London College as a Senior Lecturer in 1923. Eventually he retired in 1960 as the Professor and Head of Chemistry at Bedford College, having moved there in 1928. He was elected to the Fellowship of the Royal Society in 1939 (Ingold, 1968).

INTERLUDE: DEVELOPMENTS IN RESEARCH AND THE UNIVERSITY OF SYDNEY

World War I proved to be a great spur to scientific research in the British Empire as a means of supporting the development of technology-based industries. At the outbreak of the war Britain found that Germany was far in advance in the production of many goods relevant to the war effort (Currie & Graham, 1966, p.11):

> Great Britain was rudely awakened to the fact that she had been far too dependent on Germany for her supplies of manufactured articles, chemicals and raw materials. Optical glass, magnetos, drugs and pharmaceutical preparations, tungsten and zinc smelted from ores mined in the British Empire were among the many items processed in Germany and later imported by pre-war Britain.

Remarkably, Britain was paying royalties to Krupps for fuses in shells until 1915 and the stocks of chemical glassware were so low that a national inventory was established in case there was a need to commandeer university and other supplies (Rose & Rose, 1970, p.36).

The dyestuffs industry is particularly illuminating in emphasising the lead that Germany had taken in chemical manufacture. The aniline dyes had been discovered by the British chemist, W.H. Perkin, as a young man in 1856, and his family established a company to manufacture these dyes (Edelstein, 1961). The commercial potential of the discovery was realised by German manufacturers and there was a ready supply of well-trained chemists to support their endeavours. The German developments in the area were so effective that “by 1879, Germany was producing some £2 million-worth of coal-tar products and Britain only £450,000-worth of the dyes which had been invented in Britain by a British scientist.” (Rose & Rose, 1970, p.28). A critical point was a technically-trained workforce, Britain’s science in the nineteenth century had been largely in the hands of “amateurs and gentlemen” (Rose & Rose, 1970) but technical education in Germany was much better organised (Turner, J.W., 1909). Four German chemical concerns involved in the dyestuffs industry employed over 1000 chemists each in 1914, whereas the whole British industry employed only 1500 chemists (Currie & Graham, 1966, p.11).

As a result of concern expressed by the Royal Society, the British government established an advisory committee for scientific research. Australians were quick to realise the importance of this move with Professor Orme Masson expressing his relief that politicians had realised the parlous state of British science after much urging by scientists (Currie & Graham, 1966, p.12). These developments led in Britain to the establishment of the Department of Scientific and Industrial Research (Rose & Rose, 1970, p.40) and to the formation of an Advisory Council of Science and Industry in Australia in 1916, this body being the forerunner of the CSIRO (Currie & Graham, 1966, pp.43-56). In the discussions surrounding the formation of the Advisory Council, universities were strongly consulted and it was recognised that the stimulation and coordination of research in universities was an important aim. Some of the advice received in founding the Advisory Council had strongly urged that funding and organisation of research in universities should be the principal aim of the Advisory Council (Branagan & Holland, 1985, p.18), so scientific research in universities was very much ‘on the agenda’.

There were parallel developments at this time at the University of Sydney that secured the future of research within the university. In the British tradition of science referred to above, workers often pursued their interests as a lone worker, for example Archibald Liversidge was the sole author on almost all of his many publications (Baker, 1997). In order to incorporate further research training in the science degree a four-year Honours degree was introduced in 1922 and the Master of Science degree was introduced in 1923 (Turney, Bygott and Chippendale, 1991, p.527). The other pressure which probably helped in the establishment of a research culture was the huge growth in numbers of students studying the sciences, possibly as a response to the important role science and technology played in World War I. First year Chemistry classes with an enrolment of 222 in 1909 had more than doubled by 1919 (Branagan & Holland, 1985, p.19). There was a sharp post-war increase in enrolments with the student enrolment jumping by 700 to a total of 2,764 (including 748 women) at the start of the 1919 academic year (Turney, Bygott and Chippendale, 1991, p.431). Because of the introduction of the Honours year and the research degree (M.Sc.), academic staff were able to pursue research in collaboration with research students. This probably led to an increase in output and the opportunity to disseminate influence through appointment of graduates to other institutions. Certainly, most of Burrows' publications after the early 1920s had a research student as a co-author (see Appendix).

ESTABLISHMENT

George Joseph Burrows graduated in science at the University of Sydney in 1910 with a double university medal in chemistry and in geology & mineralogy (Branagan & Holland, 1985). As an undergraduate he had undertaken a study of the water supply of Goulburn and made recommendations for the clarification of the supply (Burrows, 1909). There was a later publication on the analysis of natural waters (Burrows, 1926b) but the samples had been collected by Dr. W.G. Woolnough in 1911 and the analyses were also performed that year. He was appointed a lecturer at the University of Sydney and collaborated with Charles Edward Fawsitt, the professor from 1909 to 1946 (Branagan & Holland, 1985), on the corrosion of steel (Burrows & Fawsitt, 1911) and the decomposition of carbamide (Burrows & Fawsitt, 1914).

In his independent work Burrows appears to have shown a strong orientation toward physical chemistry, with several publications on the rates of reactions eg. inversion of sucrose (Burrows, 1914), hydrolysis of methyl acetate (Burrows, 1919b and 1921). The study of the hydrolysis of esters included a later paper on the equilibrium in such systems (Burrows, 1925). He also worked extensively on determining the volume changes associated with dissolution of solutes, eg. (Burrows, 1919a, Burrows & James, 1925 and Burrows, 1926a).

Burrows was appointed to a temporary lectureship in chemistry at the Royal Military College, Duntroon from August 1915 to April 1919. He was depressed about his academic prospects and considered resigning from his post at the University of Sydney (Mellor, 1976). Fortunately Turner arrived in 1919 and Burrows collaborated with him on coordination chemistry projects.

Their first work together was to study the composition of the nitroprussides. Turner had indicated that he intended to do some experimental work on these compounds in his response to Friend's theories of the structures of coordination compounds (Turner, 1916):

> In the case of the nitroprussides, Friend suggests a double formula. A molecular-weight determination or, better, a determination of the number of ions by the conductivity method, is necessary before such a formula can be accepted. The author hopes to examine these points when time is available for experimental work.

Presumably Burrows' skills as a physical chemist were of significant use in this initial study as there is no indication of such experience in Turner's background. Their experimental work confirmed that the nitroprussides were salts of an acid with the formula $H_2[Fe(CN)_5NO]$ as had been earlier assigned by Hofmann rather than salts of $H_4[Fe_2(CN)_{10}(NO)_2]$, as had been suggested by Friend. Rather archly the authors stated "Friend, apparently without further experimental work, proposed for potassium nitroprusside the formula ....." (Burrows and Turner, 1919). In subsequent work, they managed to isolate nitroprussic acid and alkyl derivatives of the acid (Burrows and Turner, 1921c). This work was of considerable significance and was still referenced in the major inorganic chemistry text-book in the early 1950s (Sidgwick, 1950).

As has been mentioned Turner had worked on arsenic compounds in the years of World War I and the collaborators now turned their attention to compounds of arsenic. In their first paper on arsenic compounds (Burrows and Turner, 1920) they reported work on the deeply-coloured "additive compounds" that are formed when tertiary arsines (RR'R"As) are reacted with diiodomethylarsine (CH_3AsI_2).

Burrows and Turner reasoned that the As-oxide of 1-methyl-1,2,3,4-tetrahydroarsenoline (the arsenic analogue of reduced quinoline) should be capable of resolution into its optical isomers. They prepared the compound but not in sufficient quantity to attempt the resolution of the isomers (Burrows and Turner, 1921a). They reported the successful resolution of a salt of the phenyl-α-naphthylbenzylmethylarsonium cation in the same paper. In these salts the arsenic atom is asymmetric in the same way that a carbon atom is considered asymmetric if all four groups attached are different. It was noted that racemisation was very rapid and only small molecular rotations were recorded (Burrows and Turner, 1921a). This was an important result and represented the first successful resolution for an arsenic compound. Burrows and Turner were too modest to make such a claim but mentioned that previous attempts were unsuccessful.

They also worked on additive compounds formed between tertiary arsines and the iodides of arsenic, bismuth, mercury, lead, tin, antimony and cadmium (Burrows and Turner, 1921b). The subject of their last collaboration was the preparation of certain tris(oxalato)ferrate(III) salts. They attempted to resolve the anion into its optical isomers through isolation of the cinchonine and strychnine salts but were unsuccessful (Burrows and Turner, 1921d). They noted that the resolution of tris(oxalato)ferrates had been achieved during the course of their study by Thomas.

Turner returned to England in 1921. Burrows, remaining at the University of Sydney, had been fired with enthusiasm to continue research in coordination chemistry but had not entirely lost interest in the physical chemistry of solutions he had pursued prior to Turner's arrival (Burrows & Eastwood, 1923; Burrows & James, 1925 and Burrows, 1926a). His first work in coordination chemistry, in the absence of Turner, was to study the dissociation of cyano complexes (Burrows, 1923) and oxalato complexes (Burrows & Walker, 1923) by conductimetric and cryoscopic methods.

The intention of this paper is to focus on the foundation of the Sydney School of Coordination Chemistry, so a detailed review of the subsequent work published by Burrows will not be attempted. A sense of this work will be gained from considering the full list of his publications included as an Appendix and through his Liversidge Lecture to the Royal Society of New South Wales (Burrows, 1940).

CONCLUSION

The Sydney School of Coordination Chemistry was founded because coordination chemistry was clearly a very active area in the 1910s. This claim can be substantiated by considering the activity of Werner's school in the 1910s and their marvellous achievements in elucidating the stereochemistry of coordination compounds. This work culminated in the award of the Nobel Prize in Chemistry to Alfred Werner in 1913. The importance of this decade in the development of coordination chemistry was summarised by Lawrence Bass in his preface to a book on coordination chemistry (Schwarz, 1923):

> So far as the writer is aware, there is only one monograph in English on the subject, viz., Hedley's translation (Longman's, 1911) of the Second Edition (1908) of Werner's "Neuere Anschauungen." Since the publication of this translation many fundamental contributions to the theory have been made which should be included in any study of the complex compounds.

Turner came from the synthetic tradition in chemistry and was clearly well aware of Werner's theory of bonding in coordination compounds as is demonstrated by his effective rebuttal of Friend's ideas (Turner, 1916). His expressed interest in the nitroprusssides was pursued in Sydney and his collaboration with a chemist from the physical chemistry tradition was fortuitous, given that conductimetric and cryoscopic methods were used to confirm the formula of the nitroprussides. Turner's wartime experience with arsenic compounds provided initial synthetic problems to pursue. Burrows and Turner had an early success in resolving the optical isomers of an arsonium salt, in which the cation has four different substituents (Burrows & Turner, 1921a). Having had experience in polarimetry Burrows was able to contribute to the work on the resolution of optical isomers. The study of arsenic compounds as ligands in metal complexes was a continuing theme in the Sydney School (Craig, 1972; Burrows, 1940).

Burrows had been pursuing independent research in physical chemistry until Turner's arrival in Sydney. As has been mentioned, his independent work included studying rates of reaction of hydrolysis of esters and inversion of sugars. After Turner's brief stay, and a few further physical chemistry papers, the character of Burrows' work changed to focus on the synthesis of coordination compounds. The matter of resolving optical isomers of coordination complexes that was pursued by Burrows has been a continuing theme in the 'Sydney School' with the work on complexes of sexadentate ligands by Dwyer and Lions being a highpoint (Baker, Xiao, Craig & Baker, 1999; Baker, 1999). Given that Burrows had no preparative experience in his research work, had little or no contact with coordination chemistry and had not previously dealt with arsenic compounds, Turner's influence was absolutely critical in recruiting Burrows to coordination chemistry. Burrows clearly learnt well and, as a proselyte, was effective in promoting coordination chemistry to students and colleagues.

Part of the reason for the vast influence of this school in Australian inorganic chemistry is that coordination chemistry itself was experiencing a vast resurgence on a world scale in the 1950s. Coordination chemistry was actively pursued in Australian chemistry departments after that time, so coordination chemists were in plentiful supply to take up academic appointments in the period of expansion in Australian universities in the 1950s and 1960s. An important conference on coordination chemistry was held in Sydney on 25th and 26th May, 1953. Sir Ian Wark opened the conference and his remarks serve as an excellent summary of the influence of Burrows (Wark, 1954):

> Sydney's proud position in coordination chemistry has sprung from the efforts of one man, G.J. Burrows, now dead. Probably, in the first instance, he owed something to E.E. Turner, but Turner returned to England after a short stay in Australia, and thereafter, for 25 years, Burrows devoted his whole working life to coordination chemistry. I collaborated with Burrows on a small piece of research on the aluminium salicylato complexes. One of us had expected to get salts of an acid $H[Al(C_7H_4O_3)_2]$, the other $H_3[Al(C_7H_4O_3)_3]$. Instead we got $H_2[Al(C_7H_4O_3)_2(OH)(H_2O)]$. Burrows was delighted that here was something new and unexpected.

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Presidential Address delivered before the Royal Society of New South Wales on 5th April 2000.

(Manuscript received 26.4.2000)

APPENDIX

Following is a complete listing of the publications of George Joseph Burrows. All papers have been sighted in the original journal and confirmed through Chemical Abstracts.

1. G.J. Burrows, Notes on Goulburn water with some experiments on its clarification. *Journal and Proceedings of the Royal Society of New South Wales*, **43**, 394-8 (1909).
2. G.J. Burrows and C.E. Fawsitt, Observations on the corrosion of steel in water. *Journal and Proceedings of the Royal Society of New South Wales*, **45**, 67-75 (1911).
3. G.J. Burrows and C.E. Fawsitt, Decomposition of carbamide. *Journal of the Chemical Society*, **105**, 609-23 (1914).
4. G.J. Burrows, Inversion of sucrose by acids in water-alcohol solutions. *Journal of the Chemical Society*, **105**, 1260-70 (1914).
5. G.J. Burrows, Volume changes in the process of solution. *Journal and Proceedings of the Royal Society of New South Wales*, **53**, 74-99 (1919).
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9. G.J. Burrows and E.E. Turner, A new type of compound containing arsenic. *Journal of the Chemical Society*, **117**, 1373-83 (1920).
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13. G.J. Burrows, The rate of hydrolysis of methyl acetate by hydrochloric acid in solutions containing sucrose. *Journal of the Chemical Society*, **119**, 1798-1802 (1921).
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18. G.J. Burrows and F. Eastwood, Molecular solution volumes in ethyl alcohol. *Journal and Proceedings of the Royal Society of New South Wales*, **57**, 118-25 (1923).

19. G.J. Burrows, Equilibrium in the system methyl acetate-water-methanol-acetic acid. *Journal of the Chemical Society*, **127**, 2723-8 (1925).

20. G.J. Burrows and A.E. James, Molecular solution volumes and association. *Journal and Proceedings of the Royal Society of New South Wales*, **59**, 223-9 (1925).

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Thesis Abstract: Geology And Geochemistry of The Wallendbeen Area, N.S.W.

IAN COOPER

Abstract of a Thesis Submitted for the Degree of Master of Science,
University of Sydney 1998

The geology of the Wallendbeen area (400km south west of Sydney) is dominated by the Silurian Young Batholith and (?)Cambro-Ordovician Jindalee Group. The Jindalee Group consists of deformed and metamorphosed basalt, mafic volcaniclastic rocks, gabbro, ultramafic rocks, and banded quartz – Fe – Mn metachert defining an ocean floor

environment. Although samples are altered, whole rock major, trace and rare earth element data are consistent with a primary back-arc basin setting. A second association within the Jindalee Group is composed of finely bedded quartzose psammite and psammopelite that bear similarities to the Middle Ordovician Wagga Group. These quartzose rocks have been derived from a continental source and are part of an extensive turbidite fan covering the Lachlan Orogen in the Ordovician.

Both the mafic and quartzose rocks share a common metamorphic and structural history that involves two periods of tight to isoclinal folding. The first deformation event is correlated with the Early Silurian 'Benambran Orogeny' where peak metamorphic conditions are transitional to amphibolite facies at ~500°C and 300 MPa, indicating a depth of burial of 10 – 12 km. The second deformation involves tight to isoclinal upright folding with lower greenschist facies conditions. This event is ascribed to the 'Bowning Orogeny' that is constrained to the period ~420 to 417 Ma in the Wallendbeen area.

An 8 km long fault bounded wedge of andesitic volcanic rocks (Yandilla Volcanics) occurs within serpentinites at 'Fontenoy'. The Yandilla Volcanics comprise andesitic volcanic rocks, phyllite, banded chemical sedimentary rocks and a small hornblende diorite. The whole rock major, trace and rare earth element geochemistry display a continental arc signature and the Yandilla Volcanics are correlated with the Mid-Silurian Blowering Formation in the Cullinga area.

Both the Jindalee Group and the Yandilla Volcanics show the effects of contact metamorphism and boron-potassium metasomatism due to intrusion of the Young Granodiorite that postdates 'Bowning Orogeny' deformation. The Young Batholith is a large granitic body (210 km north-south by 40 km east-west) that is characterised by peraluminous S-type geochemistry. The intrusion is dominated by grey biotite granodiorite with rare alkali feldspar leucogranite. Metasediment xenoliths and tonalitic igneous enclaves that represent frozen droplets of a more mafic magma are abundant. Tectonic discriminant diagrams and palaeogeographic reconstructions indicate a volcanic arc setting for the pluton. The Young

Granodiorite is the product of partial fusion of Cambrian oceanic crust (Jindalee Group equivalents) and Ordovician metasediment with a mantle subduction component.

The tectonic development of the region commenced with the formation of a (?)Cambrian back-arc basin containing the Jindalee Group. This oceanic crust was covered by an enormous turbidite fan in the Ordovician, then both units were strongly deformed and metamorphosed in the Early Silurian 'Benambran Orogeny' that produced continental thickness crust. Mid Silurian back-arc transtensional rifting exhumed the Jindalee Group from ~12 km. Continental arc volcanism above the Young Granodiorite produced the Blowering Formation and Yandilla Voleanics. These units along with the Jindalee Group basement were deformed by the 'Bowning Orogeny' just prior to intrusion of the Young Granodiorite into the upper crust.

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Annual Report of Council

For the Year Ended 31 March 2000

PATRONS

The Council expresses its gratitude to his Excellency the Honourable Sir William Deane AC, KBE, Governor General of the Commonwealth of Australia, and to his Excellency the Honourable Gordon Samuels AC, CVO, Governor of New South Wales, for their continuing support as Patrons ofthe Society.

MEMBERSHIP

The membership of the Society as of 31 March 2000 comprised; Patrons 2, Honorary Members 13, Members 258, Associates and Spouse Members 24. Two members resigned and 14 members were admitted during the year. The death of the following long standing members were announced [the year of their election to the Society is in brackets]: Mr Timothy K. Wright (1994), Dr E.D. McCarthy (1949), and Prof. S.C. Haydon(1965).

OFFICE

The Society continued during the year to lease for its office and library a half-share of Convocation House, 134 Herring Road, North Ryde, on the Campus of Macquarie University. Council is thankful to the University for continuing the lease. Mrs Chandler, Assistant Office Secretary, having provided excellent service to the Society for nine years, resigned in October.

MEETINGS

Eight General Monthly meetings, six Special Monthly Meetings and Events and the 132nd Annual General Meeting were held in Sydney during the year. Eleven meetings were held by the Southern Highlands Branch. None were held by the New England Branch. Council held eleven meetings at the Society's Office at North Ryde.

PUBLICATIONS

Journal

Volume 132, Parts 1 – 4, of the Journal and Proceedings of the Royal Society of New South Wales were published for the year 1999. The volumes contained the 50th Clarke Memorial Lecture, The Presidential Address, four peer reviewed research papers, eleven abstracts of higher Degree theses, a book review, the Council Report for 1998, the Financial Statement for 1998, biographical memoirs and citations for awards for 1998.

Council wishes to thank all the voluntary referees who assessed papers offered for publication. Several permissions for reproducing material from the Society's Journal were granted.

Bulletin

Nine issues of the Bulletin were produced. The Council wishes to thank the many contributors. Particular thanks are extended to Ted O'Keeffe for production of the Bulletin and to those who assisted with the mailing.

LIBRARY

Acquisition of literature and monitoring the exchange and gifts agreements was continued at the Society's office at North Ryde. Council thanks Mr Karl Schmude, University Librarian, University of New England and his staff for their continued efficient care of the Society's collection in the Dixson Library.

AWARDS

The following awards for 1999 were presented at the Annual Dinner in March 2000:
The Society's Medal: Dr Daniel J. O'Connor;
The Archibald D. Ollé Prize:
    A/Prof. Anthony T. Baker;
The Clarke Medal: Prof. Richard Shine;
The Edgeworth David Medal:
    Dr Merlin Crossley;
The James Cook Medal: Dr Peter Colman;

The Royal Society's Studentships:
Ms Alison Basden and Ms Sharon Downes.

The Walter Burfitt Prize was not awarded this year.

NEW ENGLAND BRANCH

The Branch reported that further efforts were made to create a focal point for local citizens interested in science.

SOUTHERN HIGHLANDS BRANCH

The Branch enjoyed another successful year using Frensham School's Lecture Theatre as its lecture venue, maintaining an average attendance of over 75 members and visitors. Ten monthly lectures were held during the period, one of them jointly with the local branch of the Federation of University Women, and an additional ecological lecture and field trip was arranged for the benefit of the Wingecarribee Bush Fire Brigade.

ABSTRACTS OF PROCEEDINGS

7th April 1999

The 1079th General Monthly Meeting and the 132ndAnnual General Meeting were held at the Australian Museum, Sydney. The President, Dr Dan O'Connor was in the Chair and 23 members and four visitors attended. The Annual Report of Council and the Financial Statement for 1998 – 1999 were presented. Mr B. E. Holden was elected Auditor for 1999-2000.

The following awards for 1998 were announced:

Society's Medal
Dr David F. Branagan
Clarke Medal (geology)
Em. Prof. Richard L. Stanton AO
Walter Burfitt Prize
Prof. Anthony K. Burrell.

The Archibald D. Ollé Prize , the James Cook Medal and the Edgeworth David Medal were not awarded for 1998.

The following members were elected to the 1999 – 2000 Council:

President	A/Prof. A.T. Baker
Vice Presidents	Dr D.J. O'Connor Dr E.C. Potter Prof. D.J. Swaine Dr D.F. Branagan Prof. W.E Smith
Hon. Secretaries	Dr M.R. Lake Mrs Krysko von Tryst
Hon. Treasurer	Dr P.R. Evans
Hon. Librarian	Miss P.M. Callaghan
Members of Council	Mr J.R. Hardie Prof. A. Shannon Dr F.L. Sutherland Prof. R.H. Vernon Prof. P.A. Williams Prof. M.A. Wilson
New England Representative	Vacant
Southern Highlands Representative	Mr H.R. Perry.

Dr O'Connor yielded the Chair to the incoming President A/Prof. A.T.Baker, who then thanked the outgoing Council for its contribution during the preceding year. Dr O'Connor then presented his Presidential Address; "The Australian Republic and the Royal Society ofNew South Wales".

5th May 1999

The 1080th General Monthly Meeting was held at the Faculty of Science, University of Technology, Sydney. Mr Colin Nicholson and Dr Peter Cox addressed the meeting on "Challenge in the Provision of Drinking Water for Cities — Risk Management and Clever Science". Twenty one members and visitors attended.

2nd June 1999

At the 1081st General Monthly Meeting the 50th Clarke Memorial Lecture was delivered by Prof. Richard J. Arculus, Department of Geology, Australian National University, on "Origins of the Continental Crust" at the Geoscience Department of Macquarie University at North Ryde.

7th July 1999
The 1082nd General Monthly Meeting was held at the School of Physics, University of Sydney as a joint meeting with the Australian Institute of Physics, NSW Branch. Dr Murial Watt of the Photovoltaic Special Research Centre, UNSW, addressed the meeting on "Photovoltaics in Buildings".

4th August 1999
The 1083rd General Monthly Meeting was held at the Faculty of Science, University of Technology, Sydney where Prof. Len Lindoy, Department of Chemistry, University of Sydney, addressed the joint meeting with the RACI, NSW Branch, on “Art, Architecture and Engineering”. Thirty three members and visitors attended.

1st September 1999
The 1084th General Monthly Meeting was held at the Australian Museum, Sydney. Dr James Bell, Director of the Langton Centre, addressed the meeting on “Naltrexone – Faith, Hope but Little Clarity” and Dr Don Weatherburn, Director of the Bureau of Crime Statistics and Research, on “Drug Law Enforcement, Heroin and Harm Minimisation”.

6th October 1999
The 1085th General Monthly Meeting was held at the Australian Museum, Sydney. Dr John Ramshaw, Chief Research Scientist, CSIRO, addressed the audience on “Collagen-Polymer Composites” and Prof. I. Klineberg, Professor of Prosthodontics, University of Sydney, on “Osseoperception in Oral Implant Restoration”.

21st October 1999
The 1086th Meeting was held at the Frensham School in Mittagong in conjunction with the Southern Highlands Branch meeting to begin the process of implementing proposed changes to the Rules of the Society. This was followed by the 4th Poggendorff Memorial Lecture on Agriculture delivered by Professor Peter Cullen, President, Federation of Australian Scientific and Technological Societies, and Director, Cooperative Research Centre for Freshwater Ecology, on the topic “Water and Limitations to World Agriculture”. Thirty four members and several visitors attended.

3rd November 1999
The 1087th General Monthly Meeting was held at the Australian Museum, Sydney. Two prizes for student achievement were announced; Alison Basden, Department of Geoscience, Macquarie University, and Sharon Downes, School of Biological Sciences, University of Sydney. Both recipients spoke about their work: A. Basden about “Early Devonian Fish Faunas, SE Australia” and S. Downes about “Predator-Prey Coevolution in Rock-dwelling Reptiles”.

8th February 2000
The Joint Meeting of Four Societies Talk was given by A/Prof. M.J. Fulham on “511 keV Photons in Medicine”.

17th February 2000
The 1088th General Monthly Meeting was a joint meeting with the Southern Highlands Branch at the Frensham School in Mittagong. The proposed changes to the Rules of the Society were passed. The evening lecture was by Emeritus Professor Dr D.J. Mulvaney on the Archeology of Kakadu and Southwest Tasmania. Twenty six members and several guests attended.

SOUTHERN HIGHLANDS BRANCH

18th March 1999
At the Anual General meeting of the Southern Highlands Branch, the following Office Bearers were elected:

Chairman:	Mr Clive Wilmot
Vice Chairmen:	Dr K.G. McCracken, AO
	Mr Roy Perry
Hon. Secretary:	Mr David Robertson CBE
Hon. Treasurer:	Miss Christine Staubner

Committee Member:
Miss Marjorie Roberts
Liaison Officer: Mr Roy Perry.

Mr Dale Budd, Director, Public Affairs, Speedrail Group Pty Ltd, spoke on "The science of very fast trains".

15th April 1999
Mr Allan Cavanagh, a registered surveyor, Fellow and President of the Institution of Surveyors, Australia, and his wife, Mrs Delma Cavanagh, a science/maths teacher, spoke on "Mine Surveys among the Pyramids of Egypt".

20th May 1999
Dr David Malin, Principal Research Scientist, anglo-Australian Observatory, addressed the Society on "A Universe of Colour".

17th June 1999
Densey Clyne, noted naturalist and writer, spoke to a joint meeting of the Branch with the local branch of the Federation of University Women on "The Lives and Behaviour of Minibeasts".

15th July 1999
Professor John Charles Kelly, Visiting Professor of Physics at the University of NSW' spoke on "Cold Fusion and the Alchemists Dream".

19th August 1999
Paul Dyer, Artistic Director of the Australian Brandenburg Orchestra gave a talk on "The Structure of Music".

16th September 1999
Associate Professor Ahmad Shboul, of the Department of Semitic Studies at the University of Sydney, spoke on "Arabic Science and the European Renaissance".

21st October 1999
For this meeting, chaired by the President of The Society, Associate Professor A.T. Baker, see the record of the 1086th General Monthly Meeting, above.

29th October 1999
Dr Malcolm Gill of the CSIRO Division of Plant Industry's Centre for Plant Biodiversity Research at the Australian National Herbarium, addressed a joint meeting of the Branch with the Wingcarribee Bush Fire Brigade on the subject of "Cycles of Fire, Cycles of Life".

18th November 1999
Dr Paul Redding, A/Professor in the School of Philosophy at the University of Sydney, presented a lecture titled "Freud's Continuing Relevance for Theoretical Psychology". At this meeting the Branch's 1999 Science Award was presented to the winner, Miss Clare Roxburgh of Frensham School, Mittagong.

17th February 2000
Professor D.J. Mulvaney, AO, CGM, spoke on the "Archaeology of Kakadu and Southwest Tasmania and Lake Mungo".

16th March 2000
Dr Kirsten Benkendorff (University of Wollongong) spoke on 'Biodiversity in the Sea and its Vital Importance to Medicine".

CITATIONS FOR AWARDS

The Society's Medal 1999

Daniel John O'Connor

Daniel John O'Connor, the recipient of the Society's Medal for 1999, graduated Bachelor of Science in Chemistry at the University of Melbourne in 1949. Focussing on Mineral Chemistry, he was awarded the degree of Doctor of Philosophy, Melbourne in 1954 for a thesis on Electrical Double Layers at Mineral Solution Interfaces. Further research at Harwell, UK, and at Lucas Heights, NSW, notably on direct fluorination, produced more published work, culminating in his co-editorship of a book on the handling of radioactive materials.

In 1962 he moved into applied research, joining Colonial Sugar Refining Company at Roseville, NSW. His career there was reinforced by Bachelor and Master of Economics degrees at the University of Sydney in 1966 and 1968, Before leaving CSR in 1983, he had risen to manager of Research Laboratories.

He then returned to University life and chemical engineering at Sydney, publishing his innovative work on alumina extraction in 1988. Afterwards he was appointed Executive Director of ANZAAS (The Australian and New Zealand Association for the Advancement of Science), but it was four years later and nearing his normal retirement that ourRoyal Society began to benefit directly from his remarkably broad range of skills.

Dr O'Connor was the Society's Honorary Treasurer from 1995-1998 and our President 1998/99. He held these exalted positions with authority and distinction, and continues, through the Society's executive Council, to steer and foster the profile of the Society with his restrained but inspiring manner.

By virtue of his sustained contributions to scientific research and its management, together with his continuing role in furthering the traditional ideals of the Society, Dr Daniel O'Connor is a worthy recipient of the Society's Medal.

E.P.

The Clarke Medal for 1999

Richard Shine

Richard Shine is Professor of Evolutionary Biology at the University of Sydney. He is one of Australia's most distinguished scientists and is universally acknowledged as the leading authority on the biology of indigenous reptiles. He has made seminal contributions to his discipline both in Australia and overseas. His research on reptilian ecology has been ground-breaking, and his work has substantially clarified the ways in which microevolutionary processes determine major life-history transitions and has illuminated the ecological role played by reptiles in natural ecosystems. Two classic texts on herpetology bear witness to his expertise. Both have received Whitley awards from the Linnean Society of New South Wales.

Professor Shine has received numerous awards and has acted on several government bodies, including the Australian Research Council. A plethora of invitations to lecture at prestigious international research conferences attest his standing.

Aside from these distinguishing marks, Professor Shine has left an enduring legacy in terms of his influence on the many postgraduate students he has guided in their research. Much of their work has concerned fundamental studies of the biology of poorly-characterized Australian ecosystems and has had a major bearing on issues relating to future planning relevant to conservation and management of Australian herpetofauna.

Professor Shine is an outstanding recipient of the Clarke Medal of the Royal Society of New South Wales.

P.W.

Edgeworth David Medal for 1999

The Edgeworth David medal for 1999 is a Awarded to Dr Merlin Crossley, BSc, DPhil, Senior Lecturer in the Department of Biochemistry, The University of Sydney.

During is Honours year at The University of Melbourne, Crossley became interested in aspects of gene expression in bacteria. His postgraduate work at Oxford University and postdoctoral work at Harvard University produced important seminal findings in the area of gene transcription in mammalian cells. His study of clotting factor genes resulted in the identification of mutations that prevented the binding of two proteins to DNA. At Harvard, Crossley became interested in understanding how protein transcription factors recognise their target sites and collaborate with other proteins to control transcription. A significant outcome was the identification of another factor (FOG) that interacts with GATA-1. Dr Crossley's research has led to new insights into the molecular mechanism of promoter control in eukaryotes. It is commendable that a scientist of Dr Crossley's calibre is continuing such fundamental research in Australia.

Dr Crossley received a Rhodes Scholarship and many research grants. He teaches undergraduate courses, has Honours and PhD students and is in demand as a speaker at Conferences and research meetings. He is clearly a very active member of his Department.

Dr Crossley's contributions, especially in the field of molecular mechanisms that control the expression of human genes, confirm him as one of Australia's top molecular biologists, whose work is recognised internationally. There is no doubt that he is a very worthy recipient of the Edgeworth David Medal for 1999.

D.J.S.

James Cook Medal

Peter Colman

Dr Peter Colman is the Director of the Biomolecular Research Institute, located at Parkville Victoria. He was educated at the University of Adelaide, doing his initial research work in design of crystallographic instruments and small molecule crystallography. His introduction to protein crystallography was in Brian Matthew's laboratory, working on the structure of thermolysin, among other problems. His next theme of structural work was directed a understanding, at near atomic resolution, how the immune system functions through studying the three-dimensional structure of antibody fragments. Peter also spent some time at the University of Sydney where he worked in

Professor Hans Freeman's group on the structure of the copper-containing protein particle. The first neuraminidase structure was solved in 1983. Subsequent progress included the solution of the structure of influenza virus neuraminidase complexed with an antibody fragment. A major result of the neuraminidase work was the recognition that there is a conserved structural feature on the surface of the enzyme that could serve as a target for drugs. This led to the design of new chemical entities one of which, known commercially as Relenza, is approved in many countries for treatment of human influenza. Peter was awarded the Australia Prize in 1996 for this work.

The James Cook Medal is awarded for outstanding contributions to science and human welfare in and for the Southern Hemisphere. it is for his work on the structure of the antibodies, his fundamental work on the structure of the influenza virus neuraminidase and the subsequent development of anti-influenza drugs that Dr Peter Colman is awarded the James Cook Medal of the Royal Society of New South Wales for 1999.

A.T.B

Senior Research Studentships

This is the first time we have awarded Senior Research Studentships, which are given on the basis of doctoral research in progress.

There are two winners, namely Alison Basden from the Department of Geology, Macquarie University, for her research on "Early Devonian micro- and macro-fish faunas from south-eastern Australia", and Sharon Dpwnes from the School of Biological Sciences, University of Sydney, for her research on "Sedentary snakes and gullible geckos: predator prey in nocturnal rock-dwelling reptiles". Sharon Downes cannot be present this evening, but it is a pleasure to invite Alison Basden to come forward to receive a presentation.

A.T.B.

'Australia's Greatest Mineral Deposits' Extended Abstracts of the 23rd Annual Conference of the States' Mineralogical Societies. Broken Hill, New South Wales, June 2000

NOTICE TO AUTHORS

Manuscripts should be addressed to the Honorary Secretary, Royal Society of New South Wales, PO Box 1525, Macquarie Centre, NSW 2113. Manuscripts submitted by a non-member (through a member) will be reviewed by the Hon. Editor, in consultation with the Editorial Board, to decide whether the paper will be further considered for publication in the Journal.

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Three, single sided, typed copies of the manuscript (double spacing) should be submitted on A4 paper.

Captions to illustrations and a Table of Contents should be prepared on separate sheets.

Spelling should conform with "The Concise Oxford Dictionary"or "The Macquarie Dictionary" usage. The Système International d'Unites (SI) is to be used, with the abbreviations and symbols set out in Australian Standard AS1000.

All stratigraphic names must conform with the International Stratigraphic Guide and new names must first be cleared with the Central Register of Australian Stratigraphic Names, Australian Geological Survey Organisation, Canberra, ACT 2601, Australia. The Codes of Botanical and Zoological Nomenclature must also be adhered to as necessary.

The **Abstract** should be brief and informative.

Tables and Illustrations should be in the form and size intended for insertion in the master manuscript - 150 mm x 200 mm; column width 72 mm. If this is not readily possible then an indication of the required reduction (such as 'reduce to 1/2 size') must be clearly stated.

Maps, diagrams and graphs should generally not be larger than a single page. However, larger figures may be split and printed across two opposite pages.

The **Scale** of maps or diagrams *must* be given in bar form.

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Funeral Arrangements for Plants: An Essay in Organic Geochemistry

MICHAEL A. WILSON[1], G.S. KAMALI KANNANGARA
AND DAMIAN E. SMEULDERS

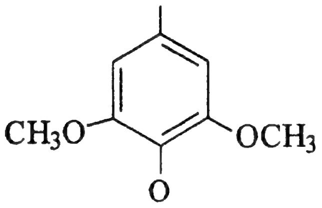
Abstract: Organic geochemistry literally is the dead end of science since it is concerned with the transformation of decaying plant material into humic substances, coal, petroleum and natural gas. The transformation process is primarily controlled by the possible degree of oxidation. Under reducing conditions coal and gas are formed and under oxidising conditions humic material is formed. Not surprisingly, the nature of the input vegetation also has an effect on the type of decomposed organic matter produced. One new finding for oxidising environments, reported here, is the concept of a host-guest structures where smaller molecules reside within a framework of a macromolecular host primarily derived from lignin. The guests within the host cannot be removed by physical separation. The structure of the host can be determined by pyrolysis gas chromatography mass spectrometry and nuclear magnetic resonance techniques. Differential thermal analysis, methylation and gas chromatography mass spectrometry and nuclear magnetic resonance data can be used to identify the guests. Some of the guests are probably held by hydrogen bonding but others are true prisoners in that they are alkanes and hence have no binding sites.

Keywords: Humic substances, Host-guest theory, COSY NMR, Differential thermal analysis

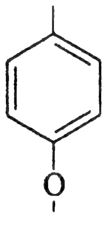
INTRODUCTION

The study of a leaf which is physically connected to a plant, belongs to the discipline of botany. For a few moments after death, while a leaf floats to the ground, the study of the mobile object belongs to the aerodynamicist, but thereafter, the leaf is the property of organic geochemists, the undertakers of the scientific world.

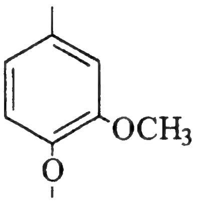
Animals contribute little to decaying matter and it is the major components of plants that are significant. These in order of importance are carbohydrates and lignin, (Figure 1) i.e. the C_3 aryl macromolecular skeletal component containing various amounts of syringyl para-hydroxyphenol or guaiacyl groups, that keeps plants upright. To a lesser extent but still important, are proteins and pigments e.g. chlorophyll (Figure 2), and also tannins and alkadiene polymers. These materials may be transposed by microorganisms and the detritus from microorganisms should not be underestimated; they too have to die.



Syringyl



para-Hydroxyphenyl



Guaiacyl

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[1] 32^{nd} Liversidge Research Lecturer

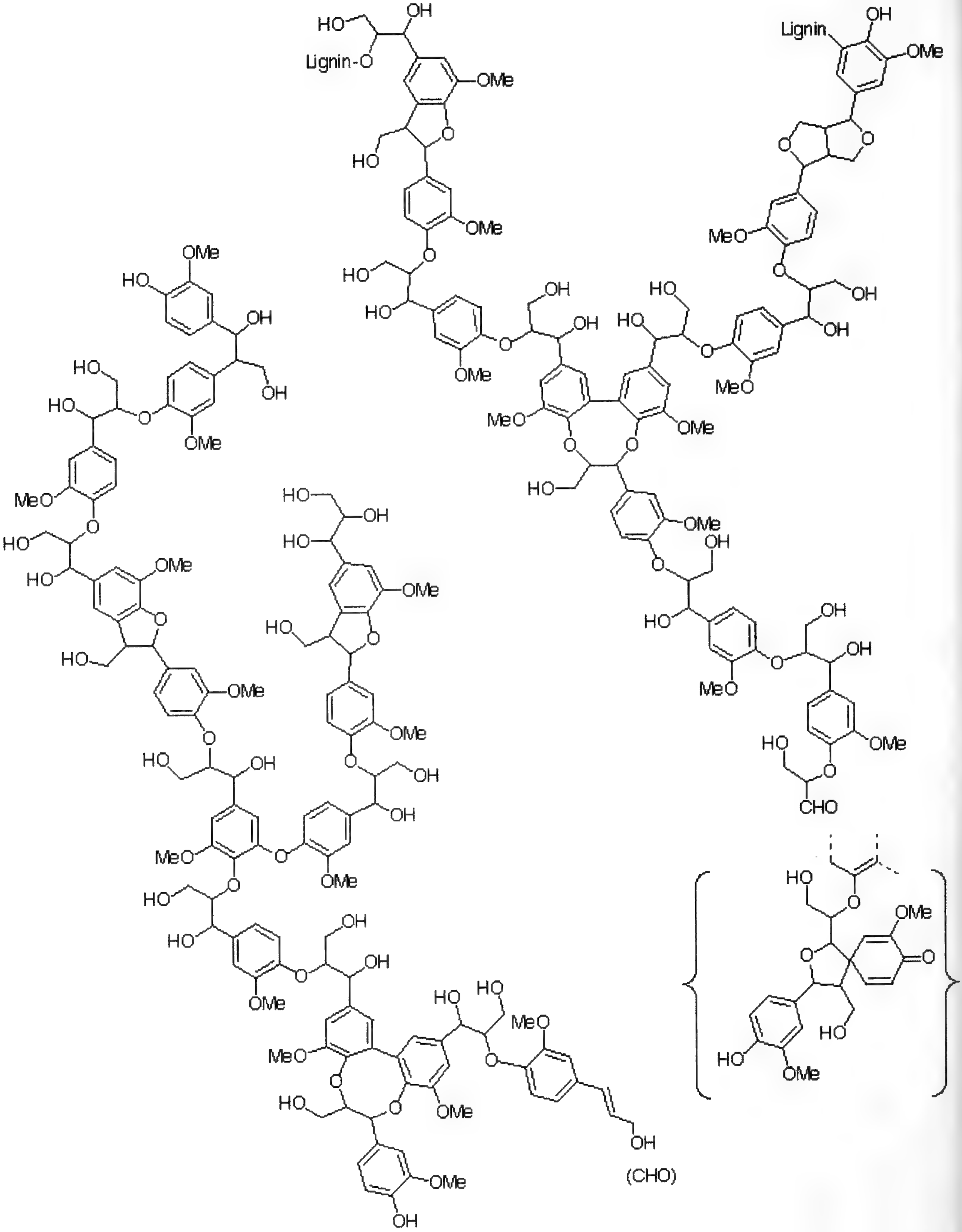

Fig. 1. Typical molecular structure of gymnosperm lignin.

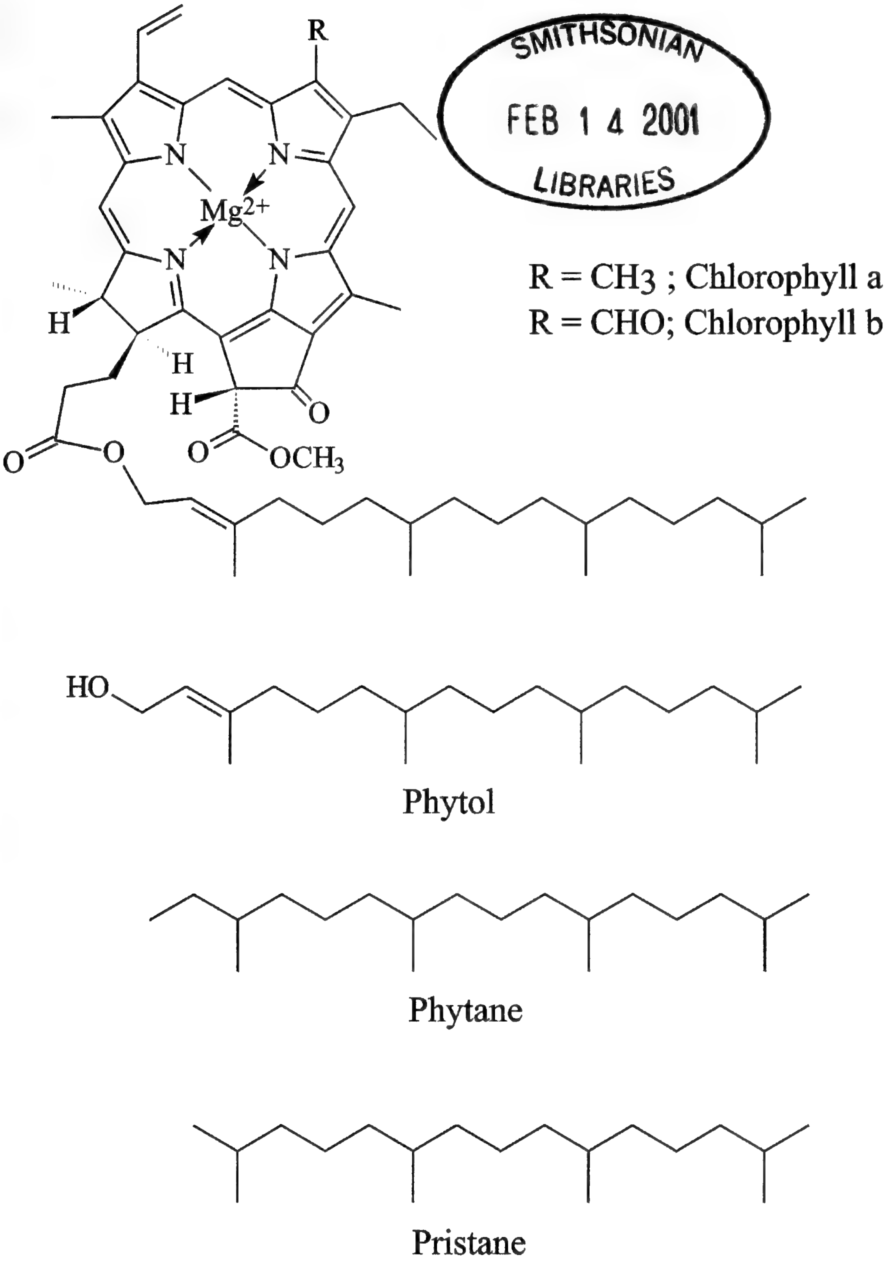

Fig. 2. Structure of chlorophyll illustrating the phytol chain. On cleavage under reducing conditions phytane is formed but on oxidation one carbon is lost to form pristane.

Once on the ground two things can happen to the leaf. It may be transposed by oxidation or by reduction. These are the great overriding chemical reactions on the planet primarily brought about by the two redox half couples:

$\frac{1}{2}\,O_2 + 2H^+ \rightarrow H_2O + 2e$ and $2H^+ + 2e \rightarrow H_2$

either directly or through biological activity.

Sometimes cyclic processes, involving both oxidation and reduction in sequence, can ensure that transformations can occur via both routes.

The limiting factor in our understanding of both oxidation and reduction processes has been the lack of methodology available for understanding the molecular structure of amorphous, non crystalline solvent insoluble organic solids. It has only been over the last twenty years with advances in appropriate instrumentation that progress has been made. Major advances have been made because of the development of three techniques. These are :

1) the development of separation methodology for high molecular weight solids (Swift, 1989),
2) the development of solid state high resolution nuclear magnetic resonance spectroscopy (NMR),
3) the development of pyrolysis gas chromatography mass spectrometry (py GC/MS).

Gel permeation chromatography and dialysis have allowed the complex macromolecules that arise from the decomposition of plants to be separated so that they can be studied. They have also allowed assessment of molecular weight and size to be determined which, with structural and elemental data, has allowed constraints on molecular formulae (Sihombing et al., 1996). Laser desorption mass spectrometry can also be useful to obtain molecular weights directly (Wilson et al., 1992). The development of nuclear magnetic resonance spectroscopy (NMR) in geochemistry (Wilson, 1987), particularly solid state NMR (for which myself, Pat Hatcher (now at Ohio State) and Caroline Preston (Forestry Canada) can claim to have contributed) has allowed some understanding of structural group composition and the nature of transformation processes. While the detail obtained on proteins is not present in ^{1}H or ^{13}C NMR spectra of these materials it is possible to estimate structural group content including the fraction of carbon which is aromatic f_a, the fraction of carbon which is carboxylic (ester or amide have usually been hydrolysed during preparation), and the fraction of carbon which is alcoholic (primarily carbohydrate). Using selected spectral editing techniques it is possible to estimate the fraction of carbon which is aromatic and protonated $f_a{}^{a,H}$, and the length of the aliphatic chains. The amounts of methoxy, phenolic anchiomeric carbohydrate and ketonic and aldehyde groups are also measurable. Two "typical" analyses are shown in Table 1 for base soluble fractions from the same soil. When combined with elemental data additional constraints on structure are imposed.

Pyrolysis gas chromatography mass spectrometry (Saiz-Jimenez and de Leeuw, 1986) is essential for structural studies because many plant decomposition substances have such high molecular weights that conventional GC/MS is almost useless and only gives us information on a very small amount of organic matter present. Pyrolysis is a method of determining structures that are components of the macromolecules. Structures that are of interest are those which can be recognised as being devised from plant building blocks. The furans derive from carbohydrates while guaiacyl and syringyl groups from lignin structures. By measuring the amounts of these in different molecular weight fractions sequencing information can be obtained.

	f_{COOH}	f_a	$f_a{}^{a,H}$	f_{OH}	$f_{phenolic}$	f_{OMe}	f_{CH_2}	$f_{aliphatic}$
Fraction 1	0.15	0.35	0.30	0.20	0.05	0.10	0.10	0.10
Fraction 2	0.30	0.15	0.30	0.20	0.05	0.20	0.05	0.10

Table 1: Fractions of carbon types in geo-organic matter produced under oxidising conditions.

REDUCTION PRODUCTS

The loose term kerogen is used to identify products under reducing conditions (Tissot and Welte, 1984). Kerogens are further divided into three groups classified on the basis of the type of organic matter involved in transformation. Type I kerogens are mainly marine algal derived and are the precursors to petroleum which is formed by further geochemical processing. Type II kerogens are from lakes and rivers. Type III kerogens are known as coal (Van Krevelan, 1993).

If the decomposition of organic matter is slowed so that macromolecules build up in the environment rather than being transformed to gas, then reducing reactions occur. Under reducing conditions the organic matter does not decay to carbon dioxide but forms peat, and, given sufficient time and pressure, brown and black coals. As expected, the carbohydrate carbon is first to go and this can be followed by high resolution solid state NMR (Figure 3). The reductive transformation of carbohydrates is complex and is not understood but a strong possibility exists that furans are formed. On reduction carbon and methane alone are not formed but coals. Coals are not carbon, nor are they unmodified plant matter. During reductive transformation of lignin, bridging groups between aromatic rings are formed. On further geological transformation from brown to black coal these bridging groups are lost (Figure 4) and the aromatic rings become less substituted until the product has about 89% carbon content. On further reduction, substantial cross linking occurs to form anthracite and then graphite (Wilson et al., 1984).

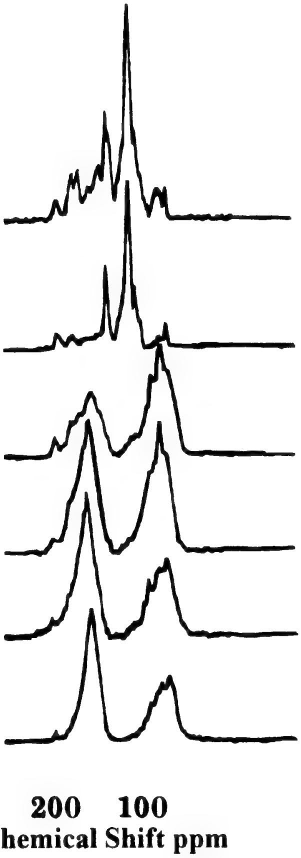

Fig. 3. ^{13}C solid state nuclear magnetic resonance spectra of fossil woods as a function of rank. The uppermost spectrum show carbohydrate resonances at 76 and 102 ppm or thereabouts as the largest two peaks. With increasing rank these are removed. The subbituminous wood (third spectrum) shows only trace amounts of carbohydrate. The lowest three spectra are from wood that is of bituminous coal rank. Note the high aliphatic carbon content centering around 30–40 ppm.

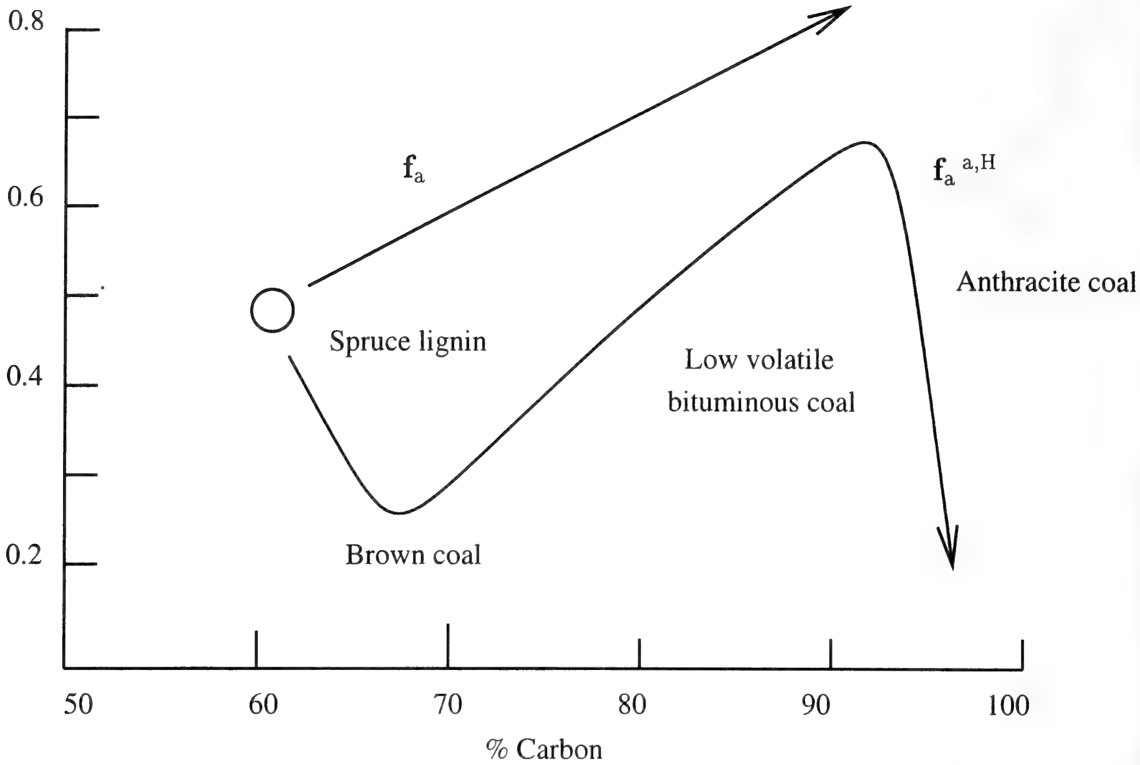

Fig. 4. Diagram to illustrate the effects that occur during coalification. Aromaticity f_a increases but the ring substitution parameter $f_a^{a,H}$ first decreases and then increases before decreasing again.

OXIDATION PRODUCTS

The loose term "humic material" is used to identify products formed under oxidising conditions. Humic materials have a number of beneficial roles in nature. They contain considerable amounts of carboxylic acid functionality, and aquatic humic materials being water soluble, have particularly high carboxylic acid contents. Some aquatic humic materials contain as much as 33% of their carbon in carboxylic acid groups (Wilson, 1987). Such structures are little more than zipped-up carbon dioxide units and it is not surprising that they are such vociferous chelating agents and can be responsible for the transport of a wide range of metal ions in soils and waters. Humic materials affect the availability of a wide range of cations and hence fertility. Their chelating role is significant in preventing run off of cations. Hence humic materials allow soils to store useful cations. (Stevenson, 1982). Their nutrient value however is restricted to slow release of nitrogen and phosphorus.

Nevertheless, humic materials are not always beneficial in industrial processing. In water they generate colour and affect taste and hence are removed during purification. The removal process can generate chloroform, which is known to be a liver carcinogen and can be present in processed waters in small amounts (Hanna et al., 1991). Furthermore, because of their chelating ability any industrial process that involves surface activity can be inhibited by humic materials. Thus they are very important in alumina processing from bauxite with sodium hydroxide. During the conversion of AlO_4^- to $Al_2O_3{\cdot}3H_2O$, the AlO_4^- ion is converted to octahedral coordination by polymerisation and addition of water groups. Humic materials interfere in this process by chelating across building sites, thereby inhibiting polymerisation and precipitation. They also inhibit the removal of oxalate, the main degradation product after extensive oxidation (Wilson et al., 1999).

The oxidative transformation of carbohydrates results in carbon dioxide, but during this process carbohydrates are rapidly consumed by microorganisms, which on death leave much of the carbon as polymethylene, presumably derived from the microorganism cell walls. A nice way to demonstrate this (Baldock et al., 1990) is by placing ^{13}C labeled glucose on a soil, and showing that the labeled carbon ends up as $(CH_2)_n$. These are also the thermal transformation products in forest fires. Carbohydrates disappear rapidly on reduction and are not present in Type I, II or III kerogens (Wilson et al., 1987) (Figure 3).

Since lignin is a major component of most but not all decaying vegetation, its transformation is also important. Depending on origin, lignin (Figure 1) may contain syringyl as well as guaiacyl and parahydroxy phenol units. During oxidative decomposition the phenolic ether linkages are believed to be broken. The resulting monohydroxy and dihydroxyphenols are believed to be relatively stable but the trihydroxyphenols can rearrange and the aryl ring can be cleaved. The authors were most surprised to find that aliphatic components are formed in this process including aliphatic carboxylic acids (Pang et al., 1990).

The eventual fate of another major plant component, proteins, is unknown. However substantial amounts of nitrogen heterocycles are found in soils and many of these do not derive from DNA or pigments (Stevenson, 1982). Of course most of the protein nitrogen can be assimilated by microorganisms as amino acids and in oxidised form as nitrates and nitrites. However in due course this nitrogen also must eventually become incorporated in complex molecules or lost to the atmosphere as NH_3, N_2O, or other gases.

Pigments are of significant interest. They yield phytol which can be transformed under reducing conditions to phytane or lose one carbon atom to form pristane in highly oxidising environments (Figure 2). Hence the pristane to phytane ratio is very useful for determining the degree of oxidation of the sediments (Didyk et al. 1978).

VEGETATION TYPE

Not surprisingly humic structure depends on vegetation type. When lignin is present the product will be quite different from that formed when it is absent. Thus Antarctic humic materials derived from moss are different from those found in dense forests (Wilson et al., 1986). Normally material formed under oak (angiosperm vegetation) differ from that formed under pine (gymnosperm vegetation) because the lignin differs. Thus the origin of the humic material can often be recognised from the macrovegetation on the soil. However if the turnover of microvegetation is more important than that of macrovegetation, microvegetation can be the major contribution to humic material and the lignin origin is unclear from examining the types of trees on the soil (Amalfitano et al., 1995).

In the absence of other factors it is possible to draw illustrative contour plots which demonstrate the effect of climate and hence microbiological activity and input vegetation on the organic matter composition produced (Wilson, 1987) (Figure 5). In principle with increased biological activity, O-alkyl carbon (as in carbohydrates) is less stable than aromatic matter which in turn is less stable than aliphatic chains. As more oxidation occurs more carboxylic carbon is also formed.

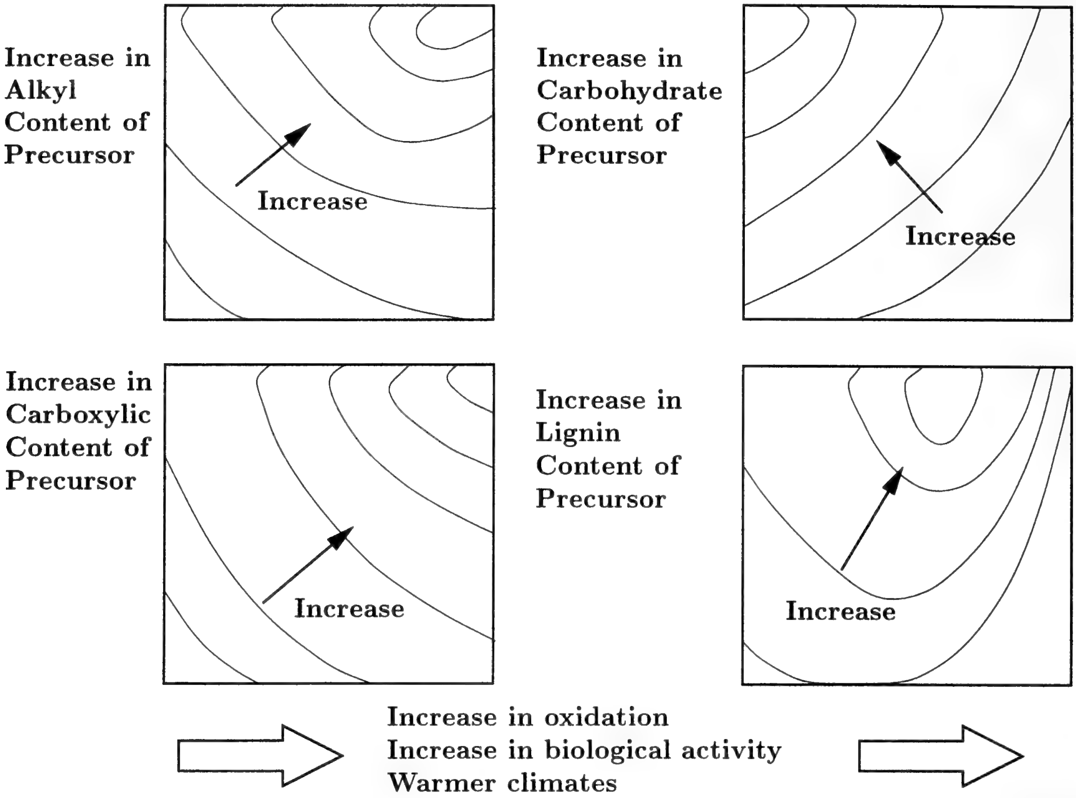

Fig. 5. Diagram to illustrate the change in functional group content of humic material with functional group content of precursor vegetation and microbiological activity.

GEOCHEMICAL PHENOMENA

Soils and sediments act via aluminosilicates and free oxides as chromatographic agents. Hence rainfall and soil composition can greatly affect the types of humic material present. In many soils organic matter is washed through the profile and behaves like eluent from a column used in chromatography. Just as in conventional chromatography, it collects on the column a distance from the initial elution point. This is normally in the B horizon of a soil, and is, in effect, a chromatographic fraction. Under rainfall some humic materials are washed into streams and rivers. That is, they are fully eluted. The process actually fractionates the organic matter.

The pH and E_h (a measure of the reduction potential) of the soil or sediment can be critical in affecting both the microbiological content as well as the potential for organic substances to be degraded or polymerised. Temperature is important here since it affects transformation rates, but temperature is most significant in fire formation. Fires are common in forests. Fire can affect the composition of humic materials by producing chars of high molecular weight polycyclic hydrocarbons (Skjemstad et al., 1996).

RESYNTHESIS

Not much is known about events immediately after decomposition. Early theories proposed that even under reducing conditions macromolecules were broken down into some sort of organic soup which was then transformed, by addition reactions, to new substances unrecognisable as original plant material. Under reducing conditions this is almost certainly now known not to be true, and it is believed many of the original macromolecules are polymerised, with and without smaller molecular weight coreactant material. Under oxidation, the situation is much more complex; probably here initial decomposition is more important, but the degree of repolymerisation is unknown and the amount of direct polymerisation has not been established. (Figure 6).

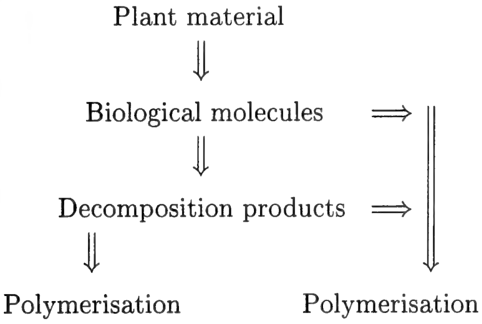

Fig. 6. Polymerisation mechanisms.

HOST-GUEST STRUCTURE

It is clear that a myriad of chemical compounds of different molecular weights compose the organic mixture that makes up the organic matter. Many have extremely high molecular weight. Values for some components as high as 300,000 Daltons have been recorded. It is also clear that this material is intimately bound with structures of relatively low molecular weight. Material of molecular weights of 50,000 Daltons or greater will have voids in its packing quite capable of occluding smaller molecular weight material, so that the smaller material are in fact guests. For organic matter produced in reducing environments ^{1}H NMR evidence was proposed (Given and Marzec, 1988) to show the existence of two groups of molecules in bituminous coals with different molecular rigidities, i.e. rigid large hosts and smaller mobile guests. Evidence for a similar structure for brown coals or lignites is based on solubility and reactivity grounds as proposed by Professor Jackson and his group at Monash University (Redlich et al. 1985). Hence it is not surprising that we have also found similar evidence for structures produced under oxidising environments.

A good example of this evidence comes from organic matter associated with bauxite which becomes soluble in sodium hydroxide used in the process for producing alumina from bauxite. Despite attempts to remove low molecular weight organic matter by dialysis, specific molecular weight fractions are obtained which still contain low molecular weight organic matter. In differential thermal analysis studies on various dialysed high molecular weight (>25,000 Da) fractions, the loss of mass up to 200°C was attributed to loss of volatile organics as well as surface and bound water (Smeulders et al., 2000). These molecules are trapped in the macromolecular matrix. This mass loss was found to be between 9.3% and 17.6%, depending on which fraction was being examined.

If the amount of water and volatile organics adsorbed on a humic extract solid is calculated and compared with that calculated by summing the amount for each molecular weight fractions adjusted for mass, the numbers differ. This shows that the water and volatile organic holding capacity for the different fractions changes when the different molecular weight materials are separated. It suggests that the various humic molecular weight fractions agglomerate together in structures where some water or volatile organic binding sites on each humic substance are held by other humic species.

This is depicted in Figure 7 (left side), where both water and small organic volatiles (circles) occupy binding sites and the bound molecules can bridge macromolecules (rectangles). After separation by dialysis (Figure 7, right side) the large molecules are separated and this process generates more sites for adsorption of small molecules. Thus the water and volatile content of the unseparated material is not the same as the mass weighted sum of the water content of the separated materials. Mass loss data expressed as first derivative plots (differential thermal gravimetric analysis, (DTG, Figure 8), indicates temperatures at which rapid mass loss occurs which allows further information to be gathered. Such plots also show that secondary volatile material is present which gives superimposed inflections in DTG plots.

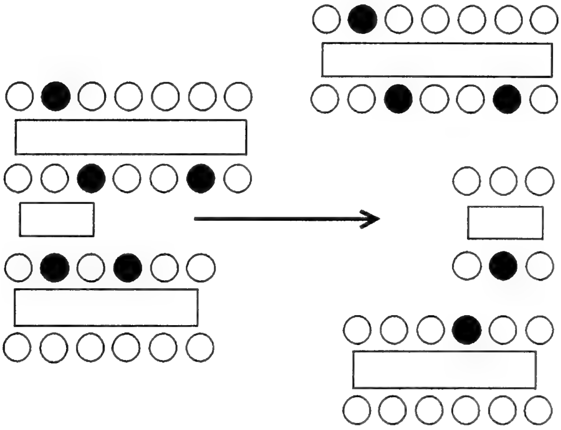

Fig. 7. Model to explain the water and volatile holding capacity of humic substances before and after fractionation. Rectangles = humic substance, length equivalent to molecular weight, ○ = water, • = organic volatile. The arrow represents the process of dialysis.

With pure compounds enthalpies can assist in identification. However, thermal events are not discrete for geo-organic matter since a variety of materials may be volatilising at the same time or changing phase in some other way. Since the ΔH of vaporisation of water is known (44 kJ mol^{-1}) (Aylward and Findlay, 1991) it should be possible to determine whether the thermal events at lower temperatures are due to loss of water or not.

It is difficult to obtain accurate values for endotherms for individual events but those below 250°C can be summed. Fractionated material produces two separate endotherms at 140°C and 210°C (ΔH = 21.69 kJ mol^{-1} if calculated as water). This is a lot lower than that expected for water (ΔH = 44 kJ mol^{-1}). Moreover a further endotherm was observed at about 250°C–272°C (see arrow Figure 9), a temperature unlikely to be due to volatilisation of bound water, and an event, which in any case, has an inappropriate ΔH. Thus there is considerable evidence for volatile material other than water being present from enthalpy data. All events are endothermic up to 250°C as expected for evaporation and are not decarboxylation reactions as they proceed well above 250°C (Vassallo and Attalla, 1992; Leinweber and Schulten, 1992). This is additional evidence that the events are evaporations which arise from trapped species and not decompositions. However, it is shown below that most of the trapped species can only be removed by methylation.

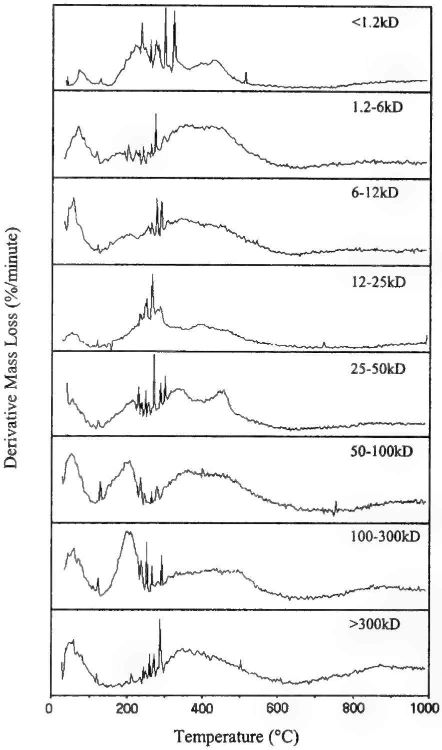

Fig. 8. Differential thermal gravimetric analysis (DTG) plots of humic molecular weight fractions

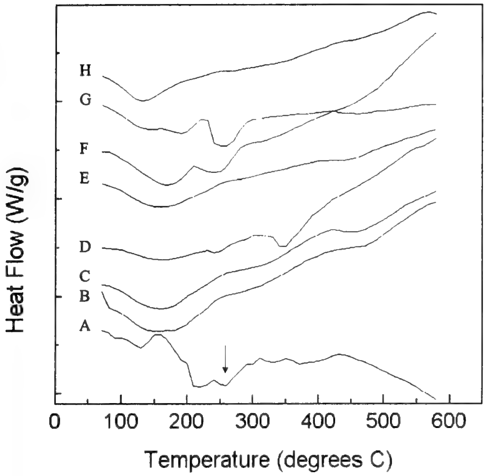

Fig. 9. Modulated Differential Scanning Calorimetry plots for humic molecular weight fractions. A = <1.2 kD; B = 1.2–6 kD; C = 6–12 kD; D = 12–25 kD; E = 25–50 kD; F = 50–100 kD; G = 100–300 kD; H = >300 kD.

^{1}H and ^{13}C NMR analysis of molecular weight fractionated material is very useful in supporting this proposition. Discrete resonances should not be observed for macromolecules, yet they are seen in high molecular weight fractions. In larger molecular weight fractions these are almost all confined to the aliphatic region. The ^{1}H NMR spectrum of all fractions of molecular weight greater than 25 kD fraction showed few discrete resonances in the aromatic region. These fractions appear to form molecular aggregates with alkanes and aliphatic fatty acids. Discrete aromatic resonances were not seen for >300 kD molecular weight fractions indicating the absence of small aromatic compounds in this fraction.

Two dimensional heteronuclear multiple quantum correlation and homonuclear chemical shift correlation spectroscopy (COSY) NMR analysis (Ruiz-Cabello et al. 1992; von Kienlin et al., 1991; Wilker et al., 1993) allowed some further information to be deduced about the fractions and identified some guests. The results from heteronuclear correlation analysis show several strong couplings in the aromatic region of the spectrum. Coupling in the aromatic region was observed between the carbon at 129.50 ppm with the proton at 8.08 ppm. The ^{1}H and ^{13}C chemical shifts suggest the compound to be benzene-1,4-dicarboxylic acid. The ^{13}C resonance at 120.49 ppm was strongly coupled to the aromatic proton at 7.55 ppm, and the carbon at 121.39 ppm was coupled to the proton at 7.96 ppm. The ^{1}H and ^{13}C chemical shifts suggest the compound to be 5-methylbenzene-1,3-dicarboxylic acid.

In the COSY aliphatic spectrum coupling was observed in the aliphatic region, with the protons in the triplet at 3.20 ppm (J = 7.6 Hz) being coupled to the protons in a quintet at 2.10 ppm (J=7.6 Hz). Integration, coupling and location of the resonances indicate that the compound contains a three-carbon alkyl chain attached to highly electronegative functional groups at each end with the two CH_2 groups adjacent to the electron withdrawing groups being equivalent. This ^{1}H NMR data is thus consistent with the compound 1,5-diphenylpentan-1,5-dione.

Several couplings were observed between protons in the aromatic region. The proton at 7.96 ppm is coupled to the strong resonance at 7.55 ppm (unresolved doublet, J = 1.4 Hz). A J coupling of 1.4 Hz suggests meta coupling. Hence the results indicate that the protons are located meta to one-another in different chemical environments on the same aromatic ring. The coupled protons located at 7.55 ppm and 7.96 ppm were the same protons observed in the ^{1}H-^{13}C 2-D NMR spectrum. The integration results show that there are twice as many protons at 7.55 ppm as there are at 7.96 ppm. The small coupling constant, integration results, and the chemical shifts, like the heteronuclear correlation experiment, also suggest that 5-methylbenzene-1,3-dicarboxylic acid is present in the 12-25 kD fraction.

If the fractions are methylated with tetramethyl ammonium hydroxide (TMAH) (Hatcher et al., 1995) and analysed by GC/MS a wide variety of compounds were identified including benzenecarboxylic acids, n-alkanes, and fatty acids. These three families of compounds represented the majority of the compounds released by the fractions. Many of the compounds released from the Bayer organic fractions by methylation were analysed as methyl esters, particularly the fatty acids and benzenecarboxylic acids.

A typical GC/MS chromatograph of the methylated Bayer organic fractions is shown in Figure 10. The chromatogram shows the large number of compounds released from the molecular weight fractions when they are methylated. Methylation with TMAH acts to release small molecules trapped in the macromolecules by forming esters and ethers with carboxylic and phenolic groups respectively, thereby breaking the hydrogen bonding that holds the molecules in place. Without methylation the molecules are held tightly in the macromolecules matrix. When the unmethylated fractions are analysed by GC/MS no small molecules are detected (Figure 10A), only the internal standard (C_{20}) is identified. This result indicates that the small molecules are tightly hydrogen bonded in the macromolecule structures by forming molecular aggregates.

With methylation n-alkanes were identified in the chromatograms with carbon chain lengths ranging from C_{11} to C_{29}. n-Alkanes are derived from algal, microbial and higher plant sources. The distribution of the n-alkanes in these fractions suggests that they were derived from the waxes of higher plants.

Fatty acids were found to be one of the main chemical classes released by the methylation of the Bayer organic fractions. Fatty acids with carbon chain lengths ranging from C_7 to C_{22} were identified as products of the fractions. Identified fatty acids were found to have both monocarboxylic and dicarboxylic acids on their structures as well as unsaturations in several of the products. Numerous C_{18} isomers were identified as products from the organic fractions. Numerous substituted benzene mono- and dicarboxylic acid compounds were identified as methylation products from the Bayer organic fractions.

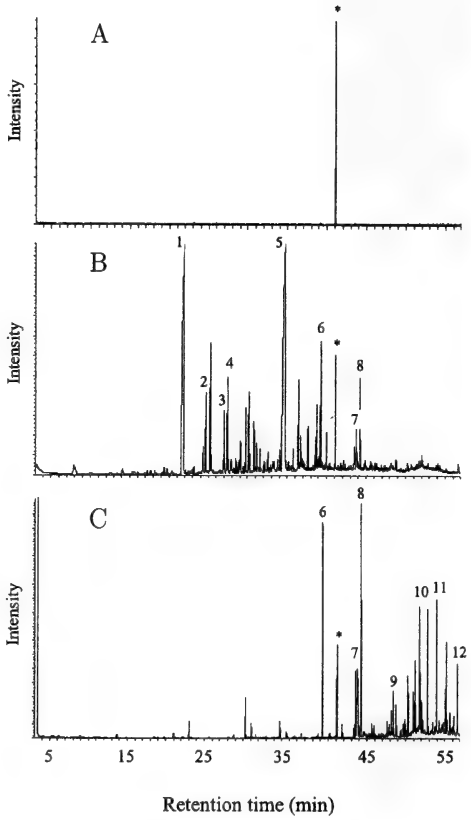

Fig. 10. GC/MS spectra of molecular weight fractions A) before methylation B) after methylation of low molecular weight humic material (<1.2 kD) and C) after methylation of high molecular weight humic material (100-300 kD). The numbering of compounds is as follows: 1) 3-Methoxybenzoic acid methyl ester, 2) 1,4-Benzenedicarboxylic acid methyl ester, 3) 1,4-Benzenedicarboxylic acid dimethyl ester, 4) 1,3-Benzenedicarboxylic acid dimethyl ester, 5) 4-Hydroxy-2-methoxy-3,6,5-trimethylbenzoic acid methyl ester, 6) Hexadecenoic acid methyl ester, 7) 7-Octadecenoic acid methyl ester, 8) 1-Octadecenoic acid methyl ester, 9) C23-Alkane, 10) C25-Alkane, 11) C27-Alkane, 12) C29-Alkane. * C20 internal standard.

It is not clear whether these host-guest complexes formed by these highly oxidised humic molecules also exist in solution. The deprotonated conjugate bases, phenoxide and carboxylate would not form strong hydrogen bonds under these conditions due to repulsion forces of similarly charged species under strongly basic conditions but under neutral pH they may still hydrogen bond. In either case, during precipitation intra molecular hydrogen and intermolecular hydrogen bonding may occur. In the process large molecular voids may be formed which could occlude other molecules. It may well be true that some of these occluded molecules also hydrogen bond but the presence of alkanes shows that for some molecules this is not always the case.

These host-guest interactions may occur in a variety of humic macromolecule compounds in the environment. It is also possible that the formation of these host-guest interactions through hydrogen bonding or physical entrapment trap other molecules including organic pollutants. While chelation of metal ions is important this may be a mechanism of breaking hydrogen-bonding intra- or intermolecular interactions which create voids or indeed a mechanism of forming other voids. Thus chelation may release guests or entrap others. The destruction of host-guest complexes might be expected to be achieved more readily than necessary for the breaking of covalent bonds. Indeed it has been demonstrated that UV radiation can degrade humic substances (Schmitt-Kopplin et al., 1998; Ong and Bisque, 1968; Havel et al.,1998; Fetsch et al., 1998; Frimmel 1998) rather than polymerise them. This reaction could be through oxidation of phenols to quinones, breaking hydrogen bonding and then subsequent release of small molecular weight guests.

SUGGESTIONS FOR FUTURE RESEARCH

Isotope ratio gas chromatography mass spectroscopy can lead to important information of the source of geo-organic compounds. A single compound can have a different isotope ratio depending on source or formation mechanism. Solid state 2 and 3 dimensional NMR will enlighten us further on coal and humic structure. New separation methodology is urgently needed.

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Minerals of the Queen Sally Mine, North-west Queensland

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Abstract: The Queen Sally deposit is located near Kajabbi, north-west Queensland. Primary cobalt mineralization comprises cobaltite and glaucodot, an assemblage that is consistent with a hydrothermal origin, possibly associated with the emplacement of the nearby Naraku granite. Oxidized cobalt mineralization consists of cobaltian calcite, erythrite and heterogenite-2H, which is unusual in that it carries up to 2.2% by weight of vanadium. Oxidation of V^{3+} in the lattice to V^{4+} may explain an early report of "blue" erythrite in the oxidized zone of the deposit.

INTRODUCTION

The Queen Sally cobalt deposit, discovered in 1922 (Anon., 1923), is situated (54411280E 7779010N) near Sally Creek, a tributary of Cabbage Tree Creek, some 4 km east of the now abandoned Cloncurry-Dobbyn railway line and approximately 13 km south-east of Kajabbi, north-west Queensland. It is one of only three mines (together with Mount Cobalt and the Success) to have recorded production of cobalt in the Mt Isa Block (Carter et al. 1961). There is little mention of the mineralogy of the Queen Sally deposit in the literature but Rayner (1938) reported the occurrence of erythrite, cobaltite, malachite, azurite, chrysocolla and a cobaltiferous "black oxide." We have had occasion to re-examine the deposit, as part of a more extensive study of the geochemistry of cobalt in the Mt Isa Block.

GEOLOGY

The ore deposit occupies a sub-vertical shear striking 155° in foliated quartzite adjacent to a narrow limestone bed, associated with cross-cutting acid pegmatite veins (quartz + orthoclase + tourmaline). Hornblende schists surround these units, and these are intruded by granite to the east and north-east (Rayner, 1938). Mine workings consist of two shafts c. 20 m deep and several shallow pits.

Primary mineralisation is confined to the pink and green stained foliated quartzite, which is well exposed in the northern shaft, and erythrite is common on a nearby cobbing floor. Quartzite on the dump carries a considerable amount of calcite, some of which is cobaltian. Careful examination of the dumps revealed an abundance of heterogenite in oxidized material and the quartzite on the dump around the southern shaft carries patches of gossan associated with scorodite, erythrite and minor secondary copper minerals.

ANALYTICAL METHODS

Polished sections of primary mineralisation and material bearing crystalline heterogenite were inspected by reflected light microscopy and then carbon coated and analysed using a JEOL JXA-8600 electron microprobe, with a beam current of 20 nA. Three wavelength dispersive spectrometers, controlled by JEOL software, and an energy dispersive spectrometer controlled by Moran Scientific software were employed for the analyses, which were calibrated against kaersutite, marcasite and pure metal standards. X-ray powder diffraction measurements were used to identify individual phases and were carried out with a Philips PW1925-20 powder diffractometer using CuKα radiation.

MINERALOGY

A list of all minerals identified in the deposit is given in Table 1. Some of the occurrences and assemblages are worthy of separate comment.

PRIMARY MINERALS

Cobaltite (analysis 3, Table 2) and related sulfosalts are the most common primary metalliferous minerals. Cobaltite, which occurs massive, in stringers and veins and as disseminated euhedral grains, is commonly associated with chalcopyrite, pyrrhotite (inclusions of which in cobaltite carry some 0.8% Co; analysis 13, Table 2), arsenopyrite, pyrite and glaucodot. Disseminated pyrite crystals are embedded in arsenopyrite and cobaltite, and pyrite is an early formed mineral (as judged by textural relationships), that contains only minor amounts of Co. Covellite carrying trace amounts of Co (analysis 15, Table 2) and chalcocite invade fractures in the primary sulfides where they have been supergene enriched. Fine-grained glaucodot commonly fills cracks in cobaltite and pyrrhotite. The arsenopyrite (analysis 6, Table 2) carries only a trace of cobalt. Chalcopyrite occurs as crystals up to 2 mm across in the foliated quartzite, in veins, as inclusions in cobaltite, and in association with pyrrhotite, included galena blebs and veinlets and disseminated subhedral to euhedral 40 micron crystals of low-iron sphalerite. Analyses of chalcopyrite (analyses 1 & 2, Table 2) indicate at least two generations of mineralisation, one carrying higher amounts of Co than the other. Negligible amounts of Ni are present in this or any other analysed phase. Pyrrhotite inclusions in cobaltite are associated with chalcopyrite and glaucodot. Early molybdenite crystals embedded in cobaltite reach 20 microns in size.

This assemblage is indicative of mesothermal to hypothermal regimes (Park and MacDiarmid, 1970; Vaughan and Craig, 1978), and is consistent with the geological setting. Further, the primary mineralisation is compatible with acid hydrothermal activity, in common with other related deposits of the eastern section of the Mt Isa Block (Nisbet et al. 1983; Wyborn, 1998) and points to the nearby Naraku granite of the Eastern Fold Belt (Perkins and Wyborn, 1998) as the source of the metals. Some of the accessory minerals identified in the lode lend support to this kind of origin, as does the composition of the pegmatite intrusions nearby (Rayner, 1938).

Analyses of cobaltite and glaucodot (analyses 3–5, Table 2) reinforce a number of these conclusions. Two generations of glaucodot are clearly represented in the deposit and both are compatable with temperatures of crystallisation of around 400–500°C, by reference to the geothermometer developed by Klemm (1965), whereas cobaltite analyses suggest a lower temperature of formation of around 200°C. Several pulses of primary mineralization occurred.

ERYTHRITE

Erythrite is the most conspicuous secondary mineral in the deposit and occurs as crusts of acicular crystals to 10 mm on quartzite and heterogenite. Of particular interest is the oxymoronic report of "an earthy blue mineral simulating azurite ... it is an unusual form of the ordinary pink hydrous arseniate (erythrine)" from the Queen Sally (Saint-Smith, 1925). No material fitting such a description was identified. Dehydration of erythrite gives a blue product (Palache, et al. 1951) and it is perhaps possible that this was the origin of the earthy blue mineral noted by Saint-Smith. However, analyses of heterogenite suggest a more plausible explanation (see below).

A.	Primary rock-forming and accessory minerals	
	Albite	$NaAlSi_3O_8$
	Allanite	$(Ce,Ca,Y)_2(Al,Fe)_3(SiO_4)_3(OH)$
	Biotite	$K(Mg,Fe^{2+})_3(Al,Fe^{3+})Si_3O_{10}(OH,F)_2$
	Calcite	$CaCO_3$
	Epidote	$Ca_2(Fe,Al)_3(SiO_4)_3(OH)$
	Fluorapatite	$Ca_5(PO_4)_3F$
	Orthoclase	$KAlSi_3O_8$
	Quartz	SiO_2
	Rutile	TiO_2
	Titanite	$CaTiSiO_5$
	Zircon	$ZrSiO_4$
B.	Primary metallic minerals	
	Arsenopyrite	$FeAsS$
	Chalcopyrite	$CuFeS_2$
	Cobaltite	$CoAsS$
	Galena	PbS
	Glaucodot	$(Co,Fe)AsS$
	Molybdenite	MoS_2
	Pyrite	FeS_2
	Pyrrhotite	FeS
	Sphalerite	$(Zn,Fe)S$
C.	Secondary minerals	
	Azurite	$Cu_3(CO_3)_2(OH)_2$
	Chalcocite	Cu_2S
	Conichalcite	$CaCu(AsO_4)(OH)$
	Copper	Cu
	Covellite	CuS
	Erythrite	$Co_3(AsO_4)_2 \cdot 8H_2O$
	Goethite	$FeO(OH)$
	Hematite	Fe_2O_3
	Heterogenite-2H	$CoO(OH)$
	Malachite	$Cu_2(CO_3)(OH)_2$
	Scorodite	$FeAsO_4 \cdot 2H_2O$

Table 1: Minerals of the Queen Sally deposit, with idealised formulae.

	1	2	3	4	5	6	7	8
As	< 0.05	< 0.05	43.7	51.0	46.6	45.1	45.16	
S	34.8	34.4	20.1	16.1	17.1	19.9	19.32	34.94
Fe	29.5	29.2	1.3	25.5	15.1	34.2		30.43
Co	< 0.05	1.6	34.1	9.2	20.1	0.1	35.52	
Ni	< 0.05	< 0.05	0.3	< 0.05	0.2	< 0.05		
Cu	34.7	33.3	< 0.05	< 0.05	< 0.05	< 0.05		34.63
Sb	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05		
Zn	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05		
Total	99.0	98.5	99.5	101.8	100.1	99.3	100.00	100.00
	9	10	11	12	13	14	15	16
As	< 0.05		< 0.05		< 0.05		< 0.05	
S	32.3	32.90	54.0	53.45	38.3	36.47	30.1	33.54
Fe	2.4		46.7	46.55	59.4	63.53	0.5	
Co	0.1		0.2		0.8		0.2	
Ni	< 0.05		< 0.05		< 0.05		< 0.05	
Cu	0.7		< 0.05		< 0.05		70.3	66.46
Sb	< 0.05		< 0.05		< 0.05		< 0.05	
Zn	64.3	67.10	< 0.05		< 0.05		< 0.05	
Total	99.8	100.00	100.9	100.00	98.5	100.00	101.1	100.00

Table 2: Analyses of primary ore minerals (wt%), Queen Sally mine. 1: Low-Co chalcopyrite, average of three analyses; 2: high-Co chalcopyrite, average of two analyses; 3: cobaltite, average of 16 analyses; 4: high-Fe glaucodot; 5: low-Fe glaucodot, average of 5 analyses; 6: arsenopyrite, average of 5 analyses; 7: calculated for CoAsS; 8: calculated for $CuFeS_2$; 9: sphalerite, average of two analyses; 10: calculated for ZnS; 11: pyrite, average of nine analyses; 12: calculated for FeS_2; 13: pyrrhotite, average of two analyses; 14: calculated for FeS; 15: covellite; 16: calculated for CuS. Values denoted as < 0.05 are not included in totals.

HETEROGENITE-2H

Heterogenite-2H (confirmed by X-ray diffraction) is very common in the dump and occurs as earthy slugs, masses and coatings, veins and stringers, as well as aggregates of plates up to 3 mm across; it was one of the main Co ore minerals of the deposit (Rayner, 1938). Microprobe analyses (Table) gave an Fe_2O_3 content of no more than 0.6% in the heterogenite, but analyses of crystalline heterogenite revealed unusually high V_2O_3 contents, up to 3.2% by weight. No other phase was detected by X-ray powder diffraction and thus it is concluded that the vanadium is substituted in the heterogenite lattice. Montroseite (VO(OH)), paramontroseite (VO_2) and goethite (FeO(OH)) are isomorphous, space group *Pbnm*, while heterogenite-2H is hexagonal, space group $P6_3/mmc$ (Anthony et al. 1997). While the structures of the CoO(OH) and VO(OH) end-members of the solid solution are different, there is no chemical reason which would serve to prohibit the substitution of some vanadium in the heterogenite lattice. We do not know the origin of the vanadium, and the geochemical association is unusual, although not unprecedented in the Mt Isa Block (Wyborn, 1998).

	1	2	3
Co_2O_3	86.6	86.4	90.20
Fe_2O_3	0.6	0.4	
V_2O_3	2.7	3.2	
H_2O (by difference)	10.1	9.8	9.80
Total	100.0	100.0	100.00

Table 3. Analyses of crystalline heterogenite, Queen Sally mine.
1: Heterogenite; idealised formula $(Co_{0.960}V_{0.033}Fe_{0.007})_{\Sigma 1.000}O(OH)$;
2: Heterogenite; idealised formula $(Co_{0.957}V_{0.039}Fe)_{\Sigma 1.000}O(OH)$;
3: calc. for CoO(OH).

Oxidation of low-iron montroseite involves oxidation of V^{3+} to V^{4+} accompanied by replacement of OH^- by O^{2-} to form blue paramontroseite (Forbes and Dubessy, 1988). Thus it seems possible that the earthy blue material mentioned by Saint-Smith (1925) was a surface coating of paramontroseite formed as a oxidation product of vanadium-rich heterogenite.

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Thesis Abstract: Physical Activity, the IGF-I Axis, and Body Composition in 55 to 75 Year-old Women

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Abstract of a Thesis Submitted for the Degree of Doctor of Philosophy, University of Sydney, New South Wales, Australia.

Similar effects of human growth hormone (GH) deficiency and ageing on body composition suggest that age-related losses of bone and muscle mass and fat accumulation may be caused by reduced GH secretion.

The anabolic effects of GH are partly mediated by insulin-like growth factor-I (IGF-I), released by the liver and other tissues in response to pituitary GH secretion. As both GH and IGF-I increase acutely with exercise, stimulation of the GH/IGF-I axis represents a means whereby regular physical activity can attenuate or reverse the effects of age on bone, muscle and fat. Studies investigating this have, however, produced conflicting findings, and information on postmenopausal women is scarce.

This cross-sectional study investigated the relationships between habitual physical activity, IGF-I bioavailability and body composition in 53 healthy postmenopausal women aged 55 to 75 years. A subgroup of 28 women receiving oestrogen replacement therapy were included, to describe interactions between oestrogen and IGF-I. Subjects underwent a multi-compartment body composition assessment to define water, protein, bone mineral, fat and muscle masses (Hansen et al, 1999). Habitual physical activity pattern was determined by a semi-structured interview. Fasting serum hormone levels (IGF-I, IGF binding protein-3, acid-labile sub-unit, and oestradiol) were determined by radio-immunoassay.

The subjects were representative of Caucasian women of the same age in regard to body composition, IGF-I status, and prevalence of habitual activity. Based on regular involvement in moderate to vigorous activity, the sample was stratified into high ($n = 27$) and low ($n = 26$) activity groups. The most common activities pursued were aerobic in nature, including walking, dancing, floor exercises and swimming. Significant ($p<0.05$) age-related declines were evident in bone, muscle, physical activity, and IGF-I axis parameters. There was some accumulation of central fat with advancing age. Protein, mineral and skeletal muscle fractions of fat-free mass showed an accelerated decline after 65 years of age. Although high activity subjects had relatively more bone and muscle, but less central adipose tissue, throughout the age range, they experienced similar overall rates of change with age to low activity subjects.

Multiple linear regression showed that advancing age, increased adiposity, and a high oestradiol level impacted negatively on IGF-I levels. Physical activity level was *not* a determinant of the IGF-I axis. As expected, oestradiol status and physical activity were both positive, independent predictors of bone mass. Adiposity was also a positive determinant of bone mass. Neither age nor IGF-I were predictors of bone parameters. Both age and physical activity were independent predictors of skeletal muscle mass, such that a highly active 70 year-old had on average the same skeletal muscle mass as a less active 56 year-old woman. However, IGF-I status was *not* related to muscle mass.

These data do not show a hypothesised positive relationship between habitual physical activity and serum IGF-I parameters, or between the IGF-I axis and body composition, in postmenopausal women. The most plausible explanation for this is that *localised* factors, such as target tissue production or modulation of IGF-I, are involved in mediating the effects of physical activity on bone and muscle.

The interaction between oestradiol and IGF-I supports previous claims of a biphasic influence of oestrogen on IGF-I, whereby moderate serum oestradiol levels can increase, but high oestradiol levels can depress, IGF-I axis activity. This phenomenon should be further investigated in a longitudinal study.

The study provides strong evidence that moderate intensity, aerobic type activities can contribute significantly to the maintenance of bone and muscle in postmenopausal women. Such activities are generally acceptable to older women, and the age range studied is known to be characterised by progressive declines in bone and muscle status, with accompanying frailty and loss of independence. These activities should therefore confer significant benefits in terms of what has been coined "successful" ageing (Hansen et al, 2000) - that is, maintaining a high degree of functionality and independence in the latter part of one's life.

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Mathematical and Computer Modelling of the Human Brain with Reference to Cortical Magnification and Dipole Source Localisation in the Visual Cortex

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Abstract of Thesis Submitted for the Degree of Doctor of Philosophy, Queensland University of Technology, Brisbane, Queensland, Australia.

Mathematical and computer models are important tools that are available to investigate natural phenomena. They can be used to model many systems. In this thesis, mathematical models are developed, implemented and applied to research involving the human brain and in particular, the human visual cortex. The visual cortex constitutes a relatively large part of the cerebral cortex. It is often used in investigations of the human brain because conclusions regarding the visual cortex can be extended to other regions of the brain. Virtually all information from the visual system is recognised as first being processed by the primary visual cortex and is then passed to other regions of the brain involved in more complex processing.

The primary visual cortex has a retinoptic mapping in that one spot in the retinal visual field maps directly to a spot on the primary visual cortex. However, there is disagreement as to the amount of cortex that is allocated to the representation of central vision or other portions of the visual field. A mathematical formulation of this mapping is presented and mapping functions which transform the surface representing the retina to the surface representing the visual cortex are developed.

If the head is modelled as three concentric spherical shells and neural sources of brain activity are modelled as dipoles, then a mathematical model which incorporates biophysical properties can be used to estimate the location of sources which generate a set of electrical potentials measured on the surface of the scalp. This model is known as dipole source localisation. The forward problem, which is the predication of a potential distribution due to a given electrical source is implemented, and the inverse problem, which is to determine a dipole source that is the best generator of a given potential distribution is solved in the least squares sense. Monte Carlo simulations and mathematical analysis show that the optimum reference electrode to use in dipole analysis is a weighted version of the common average electrode. Monte Carlo simulations are also used to investigate the accuracy of confidence regions surrounding the estimated dipole parameters.

Subsequently, a methodology for modelling a region of cortex from magnetic resonance images is developed. This methodology is applied to the calcarine fissure and surrounding grey matter to produce a three dimensional surface reconstruction of the visual cortex. This model is used to provide anatomical constraints in the dipole source localisation model. These models are then applied to visual evoked potential data obtained from an experiment which uses a chromatic grating stimulus. Results reveal that these mathematical and computer models, combined with imaging and experimental approaches, elicit new information and improved results in investigations of the human brain.

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Tectonic Evolution of the Marlborough Region, South Island, New Zealand

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The tectonic evolution of the Marlborough region has been studied by application of fission track thermo-chronology and finite element (FE) methods. The region lying within the Australian-Pacific plate boundary zone is considered to have a transcurrent fault system, known as the Marlborough Faults System (MFS). The MFS is viewed as comprising secondary transforms connecting the Hikurangi subduction margin with the main Alpine Fault oblique-slip boundary. This fault system appears to have developed sequentially towards the southeast during the past 5 million years.

Based on the principles of rock mechanics and FE method, the numerical modelling results reveal that the accommodation percentage of total displacements in Marlborough is about 85% of the total plate motion. The contour of instantaneous displacements estimated by the FE modelling can be compared to the topography of Marlborough. According to the results of the FE modelling cases, the main conclusions drawn are:

- A curved fault (the Alpine Fault) resulted from a change in the plate motion vector.
- The development of the MFS reflects the continuation of tectonic rotations.
- Three secondary faults may have developed within a short period of one another.
- Uplift movements still continue.
- A pre-existing fault offset of the Alpine Fault is not a unique result in the FE modelling.

The extremely young fission track ages (< 10 Ma) in the vicinity of the Alpine Fault bend and Seaward Kaikoura Range coincide with the recent raid uplift/erosion in these areas. All the apatite ages indicate that the host rocks in Marlborough have experienced exposure to elevated temperatures in the zone of partial annealing for apatite, some of them having been reset. Except for the samples in the Marlborough Sounds region, zircon fission track ages are older than 119 Ma, reflecting that the host rocks of the samples have not experienced temperatures in the zircon partial annealing zone since the mid Cretaceous. Apatite fission track ages and mean lengths indicate that there are two major cooling events: one occurring from the early Miocene (20 Ma) and the other in the mid Cretaceous (100 Ma).

The largest amount of rock uplift (11.5 km) occurs in the area of the Alpine Fault bend. The amounts of rock uplift and denudation derived from the fission track parameters are in the range 0.7–11.5 km and 0.6–11.0 km, respectively. In the Seaward Kaikoura Range, high elevation coincides with large amounts of denudation. Compared with the region of continent-continent convergence to the south in Canterbury, the amounts of rock uplift and denudation in Marlborough are relatively small, revealing the differences between a fully developed continent-continent collision zone and the continental transform setting in Marlborough.

The horizontal movements determined by the FE modelling can be converted into vertical movements. Both the FE modelling and fission track results show that the pattern of vertical deformation is consistent with the topography in Marlborough. The FE modelling and fission track results reveal the character of the tectonic evolution of Marlborough and are a step towards its quantification.

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Biographical Memoirs

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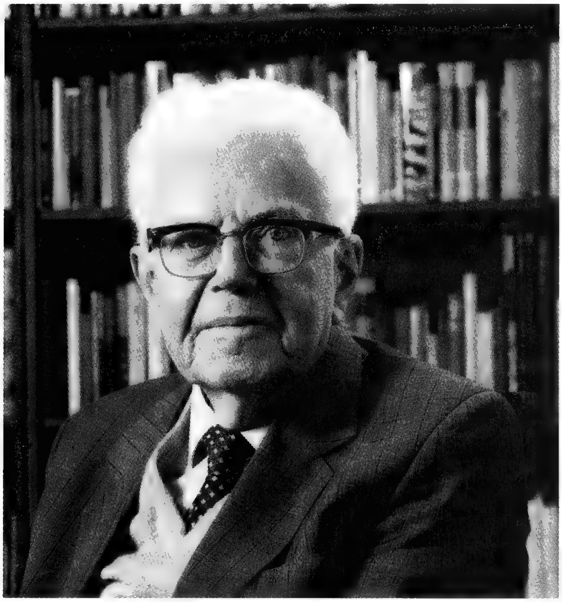

SIR MARK OLIPHANT
A Great Australian Physicist and
Philosopher (1901–2000)

Mark Oliphant, the Adelaide born nuclear physicist, thought carefully before he decided in 1949 to leave his established career in Birmingham and return, in 1950, to Australia and play a major role in the creation of the Australian National University, the establishment of the Research School of Physical Sciences, the founding of the Australian Academy of Science and the development of Canberra.

These new responsibilities left him little time to continue research, in the forefront of physics, such as he had done with Lord Rutherford in the Cavendish Laboratory at Cambridge. Work for which he was already famous and led to his election as a Fellow of the Royal Society in 1937, which, until his death on 14 July 2000, at the age of 98, made him the longest holder of a Fellowship of the Royal Society. His work with Rutherford in 1933 to 1935 had revealed the existence of tritium and helium three and demonstrated the release of energy in the fusion reaction when deuterons collided at high speed. Shortly before his death in 1937 Rutherford had proposed that Dr. Oliphant be offered the Poynting Chair of Physics at the University of Birmingham. Oliphant was reluctant to leave the then world centre of nuclear physics but was pleased to have the chance to 'run his own show'.

In Birmingham Oliphant decided to build a cyclotron to produce faster ions than any at the Cavendish Laboratory. It would be larger than the one invented by Prof. E.O. Lawrence at the University of California. Since the University could not provide the money needed, Prof. Oliphant sought grants from sponsors. Lord Nuffield gave the amount required. In October 1938 Lawrence provided details of the 60 inch diameter cyclotron that was under construction in Berkeley.

By November 1939 the 60 inch cyclotron at Berkeley was producing 10 million-electron-volt (MeV) protons and Lawrence was awarded the Nobel Prize in Physics. Writing to congratulate Prof. Lawrence, Prof. Oliphant said 'The Prize shows that the technical side of the subject is now recognised as of equal importance to the advances that follow from the use of these techniques'. This was the line Mark Oliphant followed for the rest of his scientific life, designing ever more powerful machines to shed light on the new questions that each advance raised.

Early in 1939 Oliphant was told of the need for powerful radio transmitters with a wavelength of ten centimetres or less for radio direction finding (RDF) equipment (later named radar by American engineers) small enough to fit into fighter aircraft. Because of Oliphant's experience and reputation his team at the Nuffield Laboratory won a contract with the Admiralty to identify or invent a suitable generator and detector of microwaves. Existing klystrons and magnetrons were low power laboratory devices. In November 1939 it was proposed to buid magnetrons with the tuning cavity cut into the inner copper walls of the valve was proposed. Professor Oliphant allocated the money required to build a demonstration unit. This worked well when tested in February 1940 and by June the first sealed-off magnetrons were available for use in RDF sets. Rapid improvements increased the power to 25 kW pulses so that an airborne set could detect the periscope of a submarine.

Prof. Oliphant concentrated on improving the design of klystrons, which were essential for the local oscillators in the heterodyne microwave receivers of the signals reflected from the target.

Thousands of magnetrons and klystrons were produced in England and then in USA where English designs were improved for use in American radar sets. Detailed information on the design and production was carried by Oliphant himself to America. He crossed the Atlantic several times in the empty, except for extra fuel tanks, bomb-bay of the aircraft.

On a trip in August 1941 he was asked to explore whether any attention had been given to reports from Britain on the use of uranium for the production of power and the possibility of producing a powerful bomb using U^{235}. He found that the Chairman of the 'Uranium Committee' had not read the reports nor distributed them to the committee. He saw that failure to act on the warning that a uranium fission bomb could be built might allow Germany time to do so. Deeply worried he contacted Ernest Lawrence to urge him to convince the 'Uranium Committee' and the USA Government to take immediate action on the production of U^{235} and the development of a fission bomb.

Oliphant also told Lawrence that research at Cambridge had shown that slow neutrons could convert uranium into a new element of atomic number 94 which could be easier to split than U^{235}, thus foreshadowing the possibility of a plutonium fission bomb.

When President Roosevelt, Prime Minister Churchill and Prime Minister Mackenzie King met secretly in August 1943 to sign an agreement to share all work on the development of nuclear bombs, Dr. Oliphant took a leading role with the team from Britain. Now part of the Manhattan Project, he chose to work with Lawrence in Berkeley on the large scale electromagnet separation of the uranium isotopes. Based on the research at Berekely, the extremely large separators, 'Calutrons', were built at Oak Ridge, to process the uranium in which the proportion of U^{235} had been increased by gaseous diffusion.

The magnets of the calutrons contained over 50,000 tons of steel and since copper was required for other uses, the coils of the magnets were wound, at Oliphant request, with 14,000 tons of silver from Fort Knox. Dr. Oliphant was driven to work relentlessly by the fear that Germany would produce a nuclear bomb before the Allies did, and that England would be forced to surrender to Hitler. Even with the concerted effort of the scientists and industry the isotope separators did not produce much U^{235} until November 1944. It took until June 1945 to produce sufficient to construct a test explosive assembly.

Prof. Oliphant, now back in Birmingham, was informed of the success of the test on 16 July 1945, but having ceased work in the Manhattan Project he could not participate in the final debate on how the weapon would be used. Earlier in the program it was understood that, if and when a nuclear weapon was produced, its existence and devastating power would be demonstrated to the Axis Powers before it was used against a military target, unless the demonstration itself already had lead to a cease fire.

In July 1945 the war in Europe was over, Germany had not produced a nuclear bomb, and Japan had not built one. Many of the scientist with whom Prof. Oliphant had worked were opposed to what had been intended as a defensive safeguard being used as an offensive weapon against a target in a populated area. The act of doing so horrified Oliphant and branded America as the power which set the precedence of using such an inhumane weapon. Throughout the rest of his life Prof. Oliphant advocated, with Lord Russell and many others, effective international agreements and controls to prevent the construction of nuclear weapons.

No doubt Dr. Oliphant had done more than anyone to initiate and drive the effort to build a nuclear bomb before Germany. When that threat had passed the weapons had been used in a way that horrified Oliphant and most people. Early in 1946 the United Nations was to debate the international control of nuclear weapons at a session chaired by the Australian Minister for External Affairs, Dr. Herbert Evatt. Prime Minister Chiffley proposed that Oliphant become a technical adviser to the Australian delegation. When Russia proposed an agreement by all nations not to build nuclear weapons and dismantle all existing ones, Oliphant saw this as a way to stop the threat to mankind that he had helped to create. He, like only one or two others at the conference, knew that only two bombs existed and these could be dismantled and stored under international supervision. They could be reassembled in a few hours if the agreement was not being observed. After the production of the five bombs the production of the necessary isotopes had stopped due to technical problems. The chairman, Dr. Evatt and the conference did not support the Russian resolution and the arms race with the threat to all life on earth, that Oliphant feared, began.

With a depressing feeling of guilt for participating in the horrors of Hiroshima and Nagasaki Prof. Oliphant resumed his scientific career with typical enthusiasm and "innovativeness". Firstly, the cyclotron was to be finished, but more important to him was to find money for building such a machine to accelerate protons to velocities greater than any achieved or being attempted. While working on the Manhattan Project, he worked, in his spare time, on the design of an accelerator, now known as a proton synchrotron. In January 1945, while still in America, Oliphant wrote to the Head of the Tube Alloys project seeking money to build, in England, such a machine to accelerate protons to 1000 MeV. By July 1945 money had been allocated.

In 1944 Veksler published in Russia a paper on such an accelerator for protons and electrons, while in July 1945 in America, Edwin McMillan proposed the same principal for a machine, that he named a synchrotron, to accelerate electrons to 300 MeV. It seems that Veksler, McMillan and Oliphant had each independently invented this form of accelerator but Oliphant was the first to request and receive money to construct one.

In 1946 Prof. Oliphant was invited, as one of four highly qualified Australian academics who were working in England, to form an Academic Advisory Committee to work with the Interim Council of The Australian National University on the establishment of four research schools in this new university. The Advisers met monthly, in England, from August 1947 into 1948. Oliphant ensured that many of the features of the older English universities were adopted in the statutes of the new university and that the independent authority and responsibilities of the Directors of the research schools were established.

During 1947 Prof. Oliphant planned the Research School of Physical Sciences as he saw it and gave an estimate of the cost and running expenses for the first five years. These were high compared with the expenditure of the existing universities, but because of Oliphant's standing and Prime Minister Chifley's personal assessment of him, Chifley said whatever money was needed would be provided by the Government if Oliphant was the Director.

The dominant issue for Oliphant, when deciding to accept the Directorship, and for the Council when making the appointment was his plan to build a cyclo-synchrotron to accelerate protons to an energy of 2000 MeV (2 GeV), twice the energy of protons from the synchrotron that was being built to his design in Birmingham.

Prof. Oliphant obtained funding for the School based on the estimated cost of building the proposed accelerator and of providing for nuclear physics research using protons and deuterons with energy up to 1.2 MeV from an accelerator powered by a Cockcroft-Walton rectifier which was delivered in November 1951. Thus research, under Prof. Ernest Titterton, started long before building the cyclo-synchrotron started. Prof. Oliphant directed the rapid establishment of the Research School with the creation of Departments of Astronomy, Geophysics, Nuclear Physics, Radiochemistry and Theoretical Physics by October 1952.

By June 1953, when the synchrotron at Birmingham started operating, two others, whose construction started later, were in operation: the Cosmotron at Brookhaven accelerating protons to 3 GeV and the Bevatron at Berkeley reached 5 GeV by March 1954. Typically, Oliphant proposed an innovative change which made use of the work already done on parts of the cyclo-synchrotron to build a synchrotron to accelerate protons to 10.6 GeV. The very small staff, by world standards, set to work on the new proposal. But even with the appointment of extra staff and having made considerable progress by early 1961, it was decided that only the huge machine - a homopolar generator (HPG) with two 40 tonne rotors, being built to supply the 500 MJ of energy required to create the magnetic field for the synchrotron - would be completed. The synchrotron, if built, would not accelerate protons to the energy of those from the machine that was under construction by CERN in Geneva and therefore work on it would stop.

The HPG would be able to generate pulses of current of 1 MA lasting one second, or other wave forms to a series of experiments which would probably include the study of plasma physics. The high energy pulses could be used to produce the high temperature plasma required for nuclear fusion such as observed for the first time by Lord Rutherford and Mark Oliphant when working in the Cavendish Laboratory in 1934. To prepare for this, a small group in Prof. Oliphant's Department started in 1958 to conduct experiment on the compression of plasmas.

The generator was completed by June 1962 using jets of sodium-potassium alloy (NaK), a metal that is liquid at room temperature, to carry the megamp current from the rotors to the output connections. One half of the machine was tested. It worked without fault supplying a peak current of 1.8 MA. Prof. Oliphant had considered it necessary to use liquid metal jets because experience with solid brushes indicated that the speed of the rotor surface and the massive current would destroy them. Because of the danger of handling NaK (it ignites and produces toxic smoke when exposed to air) and the complications it added to the design, operation and maintenance of the generator, a member of the HPG team decided to test brushes made from sintered copper with about one tenth graphite.

The conditions for the small scale tests matched those in the HPG and the results showed that the copper-graphite brushes could be used. The use of such brushes in the generator required unusual configurations and sophisticated mountings with actuators to apply them to the periphery of the four rotor disks for a few seconds longer than the duration of the pulse of current. They had to make continuous contact with an almost perfect surface moving in either direction at up to 40 m/s, and not be lifted or deflected by the powerful electromagnetic forces on the connections. The brushes were required to contact the rim of the 3.6 m diameter rotor disks in a close-packed ring of 864 brushes with contact face one centimetre square.

Sir Mark Oliphant (Marcus L.E. Oliphant had been created Knight Bachelor in January 1959) approved the redesign of the HPG using copper-graphite brushes and agreed to the cost involved. He designed new bearings more robust and less elaborate than those used previously. The new bearings and brushes were tested early in 1964 and worked very well. Sir Mark must have been relieved to see that the generator was now a reliable working machine which could perform as intended, however he did not comment on the success of copper-graphite brushes. In

July 1963 he had resigned from the position of Director of the Research School of Physical Sciences to be able to devote more time to the Particle Physics Department. In July 1964 he resigned from the position of head of the Department. In an address thirteen years later - after the HPG had been used to power two high field magnets, the larger to 30 Tesla, the most powerful rail gun built to that time and the first tokamak to be built outside the USSR - he said about the brushes "Mr. Marshall has produced a remarkably successful solid-state collecting system, and for that we are very grateful."

Prof. Oliphant had often expressed disappointment at the time taken to complete the work, but he never complained that someone was not working hard enough. He accepted that his estimate of the time that would be required was wrong. He sometimes considered that this error was due to the person responsible making the design too complicated, too sophisticated, or unnecessarily well-made. After commenting to this effect, he would not veto the design but occasionally he would work on a simpler version himself. He was devoted to the maintenance of academic freedom.

As soon as a section of the design was finalised Oliphant would ensure that material and parts that would not be delivered promptly were ordered immediately. Work was rarely delayed because items were not on hand. Construction proceeded as fast as the small number of staff could do it, with no outside place to have the engineering done.

The HPG was used to power tokamaks for plasma research directed towards harnessing the power from the fusion reactions until December 1985 when it was dismantled. It remains the largest homopolar generator ever built. Beautifully engineered, reflecting the skills, ingenuity and perseverance of the men who built it, it was a remarkable achievement.

From 1950 to 1966 Prof. Oliphant did much more than just try to obtain a proton accelerator. A student, and then a member of staff of the Department of Nuclear Physics for most of that time, has written: "Other departments were established and well supported with staff and funds under his selfless guidance. It is testimony to the strength and diversity of the research vigour, within the school he founded, that non-completion of the accelerator had remarkably little effect on the perceptions of either the School or large scale research, to those outside it. While Oliphant's judgement may have been questioned, his scientific credentials, determination and loyalty to the ANU never were."

From the end of the war to the end of his life he spoke with his remarkable skill, authority, and confidence, both in public and personally to many Heads of State, against the manufacture of nuclear weapons and the threat to mankind if they were used. This cause received a major boost in 1955 when Bertrand Russell and Albert Einstein signed a manifesto on 'the tragic situation which confronts humanity' due to the possibility of a nuclear war. The Russell-Einstein Manifesto was signed by eleven world renowned scientists.

In July 1957 Lord Russell invited Oliphant and 21 other leading scientists from ten countries, including the United States, Britain, Russia and Japan, to a conference to debate the manifesto. The conference was hosted by the American millionaire Cyrus Eaton at his birthplace, Pugwash, a small fishing village in Nova Scotia, Canada. Thereafter, similar conferences known as Pugwash Conference on International Affairs were held annually in different countries. Oliphant attended most and by 1960 many governments recognised the independent attitude and constructive intentions of the Pugwash participants and the organisation.

In 1954 Prof. Oliphant initiated discussions by a group of renowned Australian scientists concerning the establishment of an Australian Academy of Science and when it was founded, he was elected "founding president".

In February 1968 Sir Mark Oliphant was asked by the Premier of South Australia, Donald A. Dunston, if he would agree to a recommendation to the Queen to appoint him Governor of South Australia. After being told that the role of Governor would not prevent him attending international science conferences, Sir Mark agreed . However, Dunston's government lost power and the new government did not agree to the appointment. In May 1970 Premier Dunston returned to office. Shortly later the incumbent Governor died and Sir Mark again was recommended to Buckingham palace. In December 1971 he was sworn in as Governor of South Australia.

As Governor Sir Mark performed his traditional duties with distinction but he continued to speak frankly about the injustice or mistakes he saw in our society. At the same time he used the opportunity to emphasise the need for peace, conservation of resources and species, the protection of the natural environment, the need to improve the conditions of our indigenous people and to respond justly to their request for land rights. In general his expressed views were endorsed by a majority of the population and most were pleased to have a Governor who was willing to speak out on important issues.

Sir Mark Oliphant (Ollie or MLO to his staff) was a modest man. At the end of the war he declined an award for his work on the development of magnetrons. He considered others working under him did more than he did to invent this device which made such a decisive contribution to winning the war.

In 1954, after 4 years in the ANU as the Director of the Research School of Physical Sciences and having taken the initiative in the establishment of the Australian Academy of Science, he considered himself 'a newcomer (the academic scene) to Australia'. This was his reason for declining, when asked if he would consent to a recommendation to the Queen that he be created a Knight Bachelor. Five years later when asked again he consented and so became a KBE in January 1959.

He was a quick thinker. In any debate he would put forward an idea. If a different idea with merit was then proposed he would quickly assess it and support it if he considered it better than his. For example when the cavity magnetron was proposed he provided the support required while he continued work on the development of klystrons. He was always thinking far ahead of the people working with him or for him, but he did not veto a proposal made by a colleague. He criticised it as a member of the team and accepted the group decision. If he felt strongly about an idea of his own he went ahead alone and invited others, who could do so, to join him.

All who worked with him were amazed at his broad knowledge of science and his grand expectations of what science could, and in time, would do. As the leader of a team he followed what he had learnt from his famous Professor and master, Lord Rutherford. Prof. Oliphant set the goals, allocated tasks with several options, and expected his men to make a choice and get on with it. Then followed frequent checks on progress and many suggestions to solve any problem.

He was kind and loyal to his staff. On one occasion when the question arose of continuing with a difficult but rewarding program that he had undertaken, he responded with the statement he could not agree to terminating the project and thereby dashing the hopes of the staff who had joined him.

He had great confidence in what science could do for humanity if mankind were cooperative and wise in applying it. To him no 'good idea' or important goal was to difficult to implement. Persistence and careful thought would overcome all obstacles.

He was a persuasive speaker. Who else could have convinced the US Treasury to provide 14,000 tons of silver from their reserves to make the conductors for the magnetic isotope separators? His command of the English language was brilliant, unlike many of us with a scientific or technical bent.

He was a risk taker, but he would not risk Germany building the first atom bomb. He risked many bomber flights across the Atlantic; he risked harming his career in nuclear physics by going to Birmingham and again when coming to Australia; he consistently risked his standing and reputation with outspoken comments on issues that were important to him and knowing the merit and importance of what he had to say.

This led a colleague to remark, "One is old when you will no longer take a risk and on that measure Mark Oliphant will never grow old". He certainly did not grow old early.

Sir Mark Oliphant did not believe in a God that did or could influence life, behaviour, or well-being of people or the occurrence of natural events. He did consider the energy and the infinite extent in time and space of the universe a phenomenon the existence of which could not be explained by our present knowledge and as such was a godlike phenomenon. He did not believe there is life after death. He did considered 'life' was a wonderful and precious thing to be cared for most diligently. He was a vegetarian. He admitted that he had made mistakes, and some may hold them against him. He hoped he would not be remembered for them, but for what he had achieved for science.

After Lord Rutherford died in October 1937, Oliphant was asked, in March 1938, to address a memorial gathering at Trinity College, Dublin. His eulogy began:

> 'We have all endured the death of the greatest figure of our age. Newton, Faraday, Maxwell, Kelvin, Rutherford... his name belongs with theirs. His pupils feel that they have lost more than a master. We have lost a friend, a confidante, a fatherly adviser. Indeed many of us feel we have lost a father'.

Now we have lost one of the sons who had followed the fatherly advice. During Oliphant's life he was too modest to agree that his name should be added to the list. Perhaps we could do so now.

Many of the dates and facts quoted above were confirmed by reference to the book 'Oliphant', published by Stewart Cockburn and David Ellyard in Association with Axiom Books Pty Ltd in 1981. The research for this book was most comprehensive and the results well documented. It contains much more information about the remarkable life of Sir Mark Oliphant.

E.K.I.

Sir Mark Oliphant was elected Honorary Member of the Royal Society of New South Wales in 1948 and was awarded the Society's Cook Medal in 1974. He was born on 8th October 1901 and died on 14th July 2000.

JAMES LANGFORD GRIFFITH

1910–1999

James (Jim) Langford Griffith, a life member and past president of the Society, died on May 12, 1999 in retirement after a long and distinguished career in teaching, research and service to the Society. He was born in the Sydney suburb of Longueville on May 17, 1910 and attended North Sydney Boys High School proceeding to Sydney University where he first graduated B.Sc with first-class honours in mathematics (1931). He subsequently qualified for the awards of Dip.Ed and M.Sc and later the B.A. from that same institution. In those times, the N.S.W. Department of Education facilitated the university education of many able students inducting them into the N.S.W. high school teaching service. Jim served with the N.S.W. Department of Education from 1932 to 1945, and lectured at the Sydney (1938–39) and Armidale (1940–44 part-time) teachers' colleges. He became a Sydney Technical College lecturer in mathematics with the Department of Technical Education in 1946 and on the formation of the now University of New South Wales transferred to the new body. He remained with the University of N.S.W. until his retirement in 1974 as Associate Professor in the School of Mathematics.

In the early days of the University he was largely responsible for the design of the many courses in mathematics, especially pure mathematics, and was, and remained, a key staff member. In those times there was no strong research tradition in some disciplines of the technical college schools. Jim has the distinction of championing research in pure mathematics in an institution otherwise having a strong applied bias. His research was concerned primarily with integral transform theory, most of his papers were published in the Society's *Journal and Proceedings* and he received the Ollé prize in 1964. He served as a consultant to the Australian Atomic Energy Commission 1967–71 and was Visiting Associate Professor at the University of Kansas 1964–65.

He joined the Society in 1952 and served on Council 1954–63, 1966–70, 1974–75, 1981–83 and was Hon. Secretary 1955–57, 1966–68, Hon. Librarian 1981-85. He was President in 1958. His contribution to the Society cannot be overstated. He was a major influence over many years and served well into retirement. He was awarded the 1971 Society medal for his contributions to science, education and the Society.

His long and varied career provided him with numerous stories from the past. Many were unusual and often they were humorous, and he told them with great relish. He was always willing to share his long experience with both colleagues and students. He was survived for a time by his wife Elsie Anne, and by his daughter.

W.E.S.

JAMES LEE HERON

1939–2000

Mr James Lee Heron, a member of the Society since 1998, died on 23rd October 2000, aged 85. Jim Heron was born in Bundaberg, Queensland, and educated in Brisbane. At the outbreak of War in 1939 he, with a group of 20 other young Australians, joined the Royal Air Force to become a Pilot. He served throughout the War in Coastal Command, operating from airfields in the UK and in Iceland and recently published a history of those other 20 young Australians.

After the War James was accepted into the fledgling British Overseas Airways Corporation, and served as a Captain. On cessation of his flying years he served the airline in a number of senior administrative posts in post-colonial

Africa and in Bangladesh.

James was an Upper Freeman of the London Guild of Air Pilots and Air Navigators, and an Associate of the Royal Aeronautical Society. He and his wife frequently attended lectures arranged by the Royal Society of NSW, both in the Southern Highlands and in Sydney.

D.R.

The Royal Society of New South Wales Council's Financial Report

Your Council members submit the following financial statements of the Society for the year ended 31 December 1999.

COUNCIL MEMBERS

The names of Council Members throughout the year and as at the date of this report are:

Prof. A.T. Baker
Dr D.F. Branagan
Miss P.M. Callaghan
Dr P.R. Evans
Mr J. Hardie
Mrs Krysko v. Tryst
Dr M. Lake
Dr D.J. O'Connor
Dr E.C. Potter
Dr A. Shannon
Prof. W.E. Smith
Dr F.L. Sutherland
Prof. D.J. Swaine
Prof. R. Vernon
Prof. P. Williams
Prof. M.A. Wilson

PRINCIPAL ACTIVITIES

The principal activities of the Society during the year were: organisation of meetings; publication of the Journal & Proceedings and the Bulletin; organisation of a Summer School for Secondary Students.

SIGNIFICANT CHANGES

No significant change in the nature of these activities occurred during the year.

OPERATING RESULT

The surplus for the year amounted to $2768.

Signed in accordance with a resolution of the members of the Committee.

[Original signed by D.J. O'Connor (Vice-President)]
President ....
[Original signed by P.R. Evans]
Hon. Treasurer ....

Dated this 29th day of March 2000

The Royal Society of New South Wales Statement by Members of the Council

In the opinion of the committee the financial statements:

1. present fairly the financial position of The Royal Society of New South Wales at 31 December 1999 and the results for the year ended on that date in accordance with Australian Accounting Standards and other mandatory professional reporting requirements.

2. at the date of this statement, there are reasonable grounds to believe that the Society will be able to pay its debts as and when they fall due.

This statement is made in accordance with a resolution of the council and is signed for and behalf of the Council by:

[Original signed by D.J. O'Connor (Vice-President)]
President ....
[Original signed by P.R. Evans]
Hon. Treasurer ....

Dated this 29th Day of March 2000

The Royal Society of New South Wales Independent Audit Report to Members

SCOPE

I have audited the financial statements, being the Statement of Income and Expenditure, Balance Sheet and Notes to and forming part of the financial statements of The Royal Society of New South Wales for the year ended 31 December 1999. The Council is responsible for the financial statements. I have conducted an independent audit of these financial statements in order to express an opinion on them to members.

My audit has been conducted in accordance with Australian Auditing Standards to provide reasonable assurance as to whether the financial statement are free of material misstatement. My procedures included examination on a test basis of evidence supporting the amounts and other disclosures in the financial statements and the valuation of accounting policies and significant estimates. These procedures have been undertaken to form an opinion as to whether, in all material respects, the financial statements are presented fairly in accordance with Australian Accounting standards and other professional reporting requirements so as to present a view which is consistent with my understanding of the Society's position and the results of its operations.

The audit opinion expressed in this report has been formed on the above basis.

AUDIT OPINION

In my opinion, the financial statements present fairly in accordance with Australian Accounting Standards and other mandatory reporting requirements the financial position of The Royal Society of New South Wales as at 31 December 1999 and the results of its operation for the year then ended.

[Original Signed by Mr B.E. Holden 29 March 2000]

B.E. Holden FCA
Chartered Accountant
Chatswood

The Royal Society of New South Wales
Income & Expense at 31 December 1999

	1999 $	1998 $
INCOME		
Membership Subscriptions	15,712	14,240
Applications for Membership	152	164
Journal Subscriptions	5,581	5,139
Reprints and Other Publications	525	545
Investment Income	6,681	5,904
Summer School	1,445	2,796
Annual Dinner	(268)	177
Other	35	0
TOTAL INCOME	29,863	28,965
EXPENSES		
Accounting and Auditing Fees	575	4,765
Bank Charges and Government Duties	118	150
Bulletin	1,765	2,121
Depreciation	474	436
Insurance	842	787
Journal & Proceedings Publication and Distribution	10,901	10,228
Miscellaneous	14	13
Monthly Meetings	727	389
Office	837	842
Provision for Doubtful Debts	1,743	1,955
Rent	2,000	2,000
Salaries	6,184	7,319
Superannuation	508	201
Telephone	407	439
TOTAL EXPENSES	27,095	31,645
SURPLUS (LOSS) FOR THE YEAR	2,768	(2,680)
Balance at 1 January	112,704	115,384
Balance at 31 December	115,472	112,704

The Royal Society of New South Wales
Balance Sheet at 31 December 1999

	Notes	1999 $	1998 $
ASSETS			
CURRENT ASSETS			
Cash	2	11,409	13.758
Receivables	3	420	1.871
Investments	4	5,641	183
TOTAL CURRENT ASSETS		17,470	15.812
NON-CURRENT ASSETS			
Investments	4	132,000	132.279
Property, Plant, & Equipment	5	17,481	15.565
TOTAL NON-CURRENT ASSETS		149,481	147.844
TOTAL ASSETS		166,951	163.656
LIABILITIES			
CURRENT LIABILITIES			
Creditors and Accruals	6	4,098	6.033
Other	7	2,701	2.624
TOTAL CURRENT LIABILITIES		6,799	8.656
NON-CURRENT LIABILITIES			
Creditors and Accruals	7	7	23
TOTAL NON-CURRENT LIABILITIES		7	23
TOTAL LIABILITIES		6,806	8.679
NET ASSETS		160,145	154.977
MEMBERS' FUNDS			
Library Reserve	8	7,311	7.311
Library Fund	9	13,909	13.173
Trust Funds	10	22,588	22.788
Studentship Fund	15	865	0
Accumulated Funds		115,472	112.704
TOTAL MEMBER'S FUNDS		160,145	154.977

The accompanying notes form part of these financial statements.

The Royal Society of New South Wales
Notes to and Forming Part of the Accounts
for Year Ended 31 December 1999

1 Statement of Accounting Policies These financial statements are a special purpose financial report prepared for use by the council and members of the Society. The council has determined that the Society is not a reporting entity.

The statement has been prepared in accordance with customary accounting practices on an accruals basis and on historic costs, taking no account of changing money values, or, except where specifically stated, current valuations of non-current assets.

Where required, comparative figures have been adjusted to conform with changes in presentation for the current financial year.

		1999 $	1998 $
2	**CASH**		
	Cash on Hand	28	68
	Cash at Bank	11,381	13,690
		11,409	13,758
3	**RECEIVABLES**		
	Debtors for contributions towards printing		
	Journal & Proceedings	420	1,871
	Membership Subscriptions in Arrears	3,834	2,653
	Less Provision for Doubtful Debts	(3,834)	(2,653)
		420	1,871
4	**INVESTMENTS**		
	Current		
	Deposits at Call	5,641	183
	Non-Current		
	St George 551324554	0	77,571
	St George 551555467	132,000	0
	Westpac Variable	0	54,708
		132,000	132,279
5	**PROPERTY, PLANT & EQUIPMENT**		
	Office equipment and furniture - at valuation of	12,390	10,000
	less accumulated depreciation	8,519	8,045
		3,871	1,955
	Library - at 1936 valuation	13,600	13,600
	Pictures - at cost less depreciation	10	10
		17,481	15,565

			1999 $	1998 $
6	**CREDITORS & ACCRUALS**			
	Sundry Creditors & Accruals		4,098	6,033
7	**OTHER LIABILITIES**			
	Current			
	Life Members subscriptions prepaid		16	16
	Membership subscriptions paid in advance		133	30
	Journal & Proceedings subscriptions paid in advance		2,552	2,578
			2,701	2,624
	Non-current			
	Life Members subscriptions - prepaid		7	23
8	**LIBRARY RESERVE**			
	Balance at 1 January		7,311	7,311
	Movement for year		0	0
	Balance at 31 December		7,311	7,311
9	**LIBRARY FUND ACCOUNT**			
	Balance at 1 January		13,173	12,325
	Donations and interest		774	868
			13,947	13,193
	Library purchases and expenses		(38)	(20)
	Balance at 31 December		13,909	13,173
10	**TRUST FUNDS**			
	Included in Trust Funds are:			
	Clarke Memorial Fund	(11)	3,291	3,166
	Walter Burfitt Prize	(12)	7,350	7,552
	Liversidge Bequest Fund	(13)	3,101	3,557
	Ollè Bequest Fund	(14)	8,846	8,513
	Total Trust Funds		22,588	22,788
11	**CLARKE MEMORIAL FUND**			
	Capital		5,000	5,000
	Revenue			
	Income		134	146
	Expenditure		(10)	(7)
	Surplus (Deficit)		124	139
	Balance at 1 January		(1,833)	(1,973)
	Balance at 31 December		(1,709)	(1,834)
	Total fund capital and revenue		3,291	3,166

		1999 $	1998 $
12	**WALTER BURFITT PRIZE FUND**		
	Capital	3,000	3,000
	Revenue		
	Income	308	350
	Expenditure	(510)	
	Surplus (Deficit)	(202)	350
	Balance at 1 January	4,552	4,200
	Balance at 31 December	4,350	4,550
	Total Fund Capital and Revenue	7,350	7,552
13	**LIVERSIDGE BEQUEST FUND**		
	Capital	3,000	3,000
	Revenue		
	Income	143	166
	Expenditure	(598)	(43)
	Surplus (Deficit)	(455)	123
	Balance at 1 January	557	434
	Balance at 31 December	101	557
	Total fund capital and revenue	3,101	3,557
14	**OLLÉ BEQUEST FUND**		
	Capital	4,000	4,000
	Revenue		
	Income	333	412
	Expenditure	0	(500)
	Surplus (Deficit)	333	(88)
	Balance at 1 January	4,513	4,601
	Balance at 31 December	4,846	4,513
	Total fund capital and revenue	8,846	8,513
15	**STUDENTSHIP FUND**		
	Revenue		
	Income	1,865	0
	Expenditure	(1,000)	0
	Surplus (Deficit)	865	0
	Balance at 1 January	0	0
	Balance at 31 December	865	0

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Membership List

The year of election is given in brackets; an asterix indicates pre-paid Life Membership. Assoc. = Associate Member. The number of papers published in the *Journal* is indicated by P. Degrees and diplomas are listed in order of seniority, with awarding institution, where known.

HONORARY MEMBERS

BENNETT, J.M. Emer. Professor AO, BE(Civ), BE(Med & Elect), BSc Qld, PhD(Camb), FACS, FBCS, FIEAust, FIMA, FRSS, MACH, MIFF, MORSA, MASOR, ACS(Hon.Life), FIS Balgowlah NSW (1978; Hon.Memb. 1995)

CAREY, S.W. Emer. Professor AO, FAA, DSc(Syd), HonDSc(PNG, FNAI, FGS Sandy Bay TAS (1938; Hon.Memb. 1976; P.2)

CORNFORTH, J.W. Emer. Prof. Sir AC, Kt, CBE, Nobel Laureate, FRS, DPhil(Oxf), MSc(Syd) Sussex England (1977)

CRAIG, D.P. Emer. Professor AO, FAA, FRACI, FRS, DSc, PhD(Lond), HonDSc, MSc(Syd),HonDrChem(Bologna), FRSChem. Canberra ACT (1941; Hon.Memb. 1985; P.7)

FIRTH, R.W. Emer. Professor Sir Kt, MA, PhD (Lond), DSc FRS England (Hon.Memb. 1952)

McCRACKEN, K.G. Dr AO, FAA, FTS, DSc, PhD, BSc, FAusIMM Mittagong NSW (1973; Pres. 1979; Hon.Memb. 1995)

NAPPER, D.H. Professor MSc(Syd), PhD(Camb), FAA, FRACI University of Sydney NSW (1973)

NOSSAL. Sir Gustav AC, Kt, CBE, FAA, FTS, FRS, HonDSc, MB, B, BScMed(Syd),HonDSc(ANU), PhD(Melb), FRACP, FRCP, FRSE Parkville VIC (Non.Memb. 1986)

ROBERTSON, R.N. Emer. Professor Sir AC, Kt, CMG, FAA, FRS, DSc(Syd), PhD(Camb). The Aust. National Univ. Canberra ACT (Hon.Memb. 1985)

STANTON, R.L. Professor FAA, PhD, MSc(Syd), HonFIMM, HonFGSAm, MAusIMM Canberra ACT (1949; Hon.Memb. 1988; P.2)

WILD, J.P. Dr AC, CBE, FAA, FTS, FRS, ScD, MA(Camb), HonDSc(ANU) Ann Arbor Michigan USA (Hon.Memb. 1990)

YERBURY, D. Emer. Professor AM, LLB(Lond), PhD(Melb), DipTechSci(Manc). Macquarie University NSW (Hon.Memb. 1996)

MEMBERS

ADRIAN, J. BSc(Syd). Blackheath NSW (1970)

AMBLER, E.P. Dr BSc(Hons) PhD. Mittagong NSW (1996)

AMBLER, W.L. BSc, LLB. Mittagong NSW (1996)

ANDERSON, G.W. BSc, BE. Lane Cove NSW (1948)

ARDITTO, P.A. BSc, MSc, Dip.Ed. Ivanhoe Vic (1981)

ARROLD, N.P. Dr BSc(Agr) PhD(Syd). Mittagong NSW (1998)

AULD, J.E. Wingello NSW (1999)

AULD, W.T.M. Wingello NSW (1999)

BADHAM, C.D. Dr MB, BS, DR(Syd), FRACR, BSc(NSW). Paddington NSW (1962)

BAGGS, S.A. Dr BArch, DipArch, MArch(NSW), Grad.Dip. Land Des, PhD. Newport NSW (1989)

BAGGS, D.W. B.Arch (Hons) NSWIT. Castle Hill NSW (1992)

BAKER, A.T. A/Prof. BSc(NSW), PhD(NSW), FRACI, C.Chim. Oatley NSW (1997; Pres.

1999)

BAKER, N.J. Oatley NSW (1999)

BANFIELD, J.E. Dr MSc, PhD Melb. Armidale NSW (1963)

BASDEN, A.M. BSc (Hons). Winston Hills NSW (1999)

BASDEN, H. BSc, Syd, DipEd Syd, MAppSci UTNSW, Collaroy Beach NSW (1970)

BASDEN, K.S. Dr BSc NSW, PhD NSW, MRACI MAusIMM, CChem, MIEAust, ASTC, CPEng, FInstE, FAIE. Lawson NSW (1951)

BEAN, J.M. Dr PhD Trangie NSW (1975)

BEAVIS, F.C. Emer. Prof. MA Camb, BSc Melb, LLB NSW, FGS, PhD Melb. Cowra NSW (1973; Pres. 1978)

BENNETT, M.R. Prof. FAA. Sydney NSW (1993)

BHATHAL, R. Dr CertEd, BSc, PhD, FS M S. Georges Hall NSW (1982; Pres. 1984)

BILLS, R.M. MB,BS Syd, Queanbeyan NSW (1982)

BINNIE, A.E. MSc(Hons), BSc, DipEd; East Ryde NSW (1998)

BINNS, R.A. Dr BSc Syd, PhD Camb, North Ryde NSW (1964)

BLACK, D.St C. Prof. MSc Syd, PhD Camb. AMusA, FRACI. Sydney NSW (1983)

BLACK, L. Broken Hill NSW (Assoc. 1975)

BLACK, P.L. OAM, BSc(NSW) Broken Hill NSW (1975)

BLANKS, F.R. AM, BSc, Greenwich NSW (1948*)

BLAXLAND, D.G. Dr MB, BS Syd, FRCPA. Wagga Wagga NSW (1977)

BRAKEL, A.T. Dr BSc, PhD Newc. Canberra ACT (1968)

BRANAGAN, D.F. Dr MSc, PhD Syd, FGS. HonMGSAus Northbridge NSW (1967; Pres. 1995)

BRIERLEY, A.J. BSc., Dip Tech., M.B.A. Lidcombe NSW (1999)

BROWN, D.J Dr DSc, DPhil O'Connor ACT (1942*)

BROWN, H.E. MSc Epping NSW (1975)

BROWN, L.M. Dr PhD, BSc(Hons). Thirlmere NSW (1999)

BURGESS, J.R. Dr B.Med.Sci, M.B., B.S., M.D., FRACP. Hobart TAS (1999)

BURNS, OBE B.B. OBE, MDS Syd, FICD. Collaroy NSW (1961)

BURNSTEIN, K. M. Des Bowral NSW (Assoc. 1997)

BURNSTEIN, R. M.Sc M.B.A. Bowral NSW (Assoc. 1997)

CALLAGHAN, P.M. Bsc Syd, MSc Melb, ALAA North Sydney NSW (1984)

CALLENDER, J.H. BSc NSW, MSc(Hons), Woll'g, Wahroonga NSW (1969)

CAMPBELL, I.G.S. BSc, Wahroonga NSW (1955)

CAMPBELL, K.S.W. Emer. Prof. MSc, PhD Qld, FAA. Campbell ACT (1975)

CAMPBELL, M.T. Dr Picton NSW (1994)

CAVILL, G.W.K. Emer. Prof. Seaforth NSW (1944)

CHAFFER, E.K. Chatswood NSW (1954*; Pres. 1975; P.1)

CHALMERS, R.O. ASTC. Cleveland QLD (1933*)

CHATFIELD, S.P. Lane Cove NSW (1988)

CHAUDHRY, T.M. Minto nSW (1996)

CHOPIN, L.K Dr BVSc(HONS), AMusA., PhD Oakey QLD (1997)

CLANCY, B.E. Dr MSc, PhD NSW, DipEd Syd, Lugarno NSW (1957)

CLEMENTS, M.A. Dr Chisholm ACT (1997)

COENRAADS, R.R. Dr BA (Hons) Macq, MSc Brit.Columbia, PhD Macq, Frenchs Forest NSW (1991)

COLE, E.R. Dr MSc Syd, PhD NSW, FRACI. Eastwood NSW (1940)

COLE, J.M. BSc(Hons) Syd, Eastwood NSW (1940)

COLE, T.W. Professor FTS, BE WA, PhD Camb, FIEAust, University of Sydney NSW (1978)

COLLETT, G.W. BSc, DipEd Syd, ARACI. Cherrybrook NSW (1940)

COOK, J.L. Dr BSc, MSc, PhD NSW, FAIP, MAPS. Caringbah NSW (1990)

COPLAND, B.J. Moss Vale NSW (1994)

CORBYN, J.A. Dr PhD Lae PNG (1999)

COX, C.D. BSc, DipEd Qld, Forestville NSW (1964)

CRADDOCK, D.A. BSc (Eng) Epping NSW (1999)

CRASS, J.K. Dr MAppSc, PhD(UTS), West Pymble NSW (1998)

CREELMAN, R.A. Dr BA, MSc(Hons), PhD Macq, Epping NSW (1973)

CROOK, K.A.W. Dr MSc Syd, PhD NE, BA ANU. Hawaii USA (1954)

DAGGETT, C. Moss Vale NSW (Assoc. 1998)

DAGGETT, D.G. Moss Vale NSW (1998)

DAVIES, AO L.W. Prof. AO, BSc(Syd), DPhil(Oxon),FIEEE,FTSE, FAA. Picton NSW (1997)

DAVIS, B.J. B.A.(Syd), Diplome de Medaille d'or Brussels. Neutral Bay NSW (1998)

DAY, A.A. Dr BSc Syd, PhD Camb, FGS, FAusIMM. Lindfield NSW (1952; Pres. 1996)

DOWNES, S.J. BSc (Hons) Univ. Melb University of Sydney NSW (1999)

DRAKE, L.A. Dr BA (Hons), BSc Melb, MA, PhD CALIF, LA PAZ, Bolivia (1962)

EMMETT, A.J.J. Dr MB. BS. FRCS. FRACS.. Bowral NSW (1999)

ENGEL, B.A. Dr MSc NE, PhD, Uni. of Newcastle NSW (1961)

EVANS, P.R. Dr BA Oxf, PhD Brist, MAIG. Turramurra NSW (1968)

FACER, R.A. Dr BSc(Hons), PhD Syd, FausIMM, MGSAus, MAGU. North Turramurra NSW (1965)

FELTON, E.A. Dr BSc ANU, FGM. Eden NSW (1977)

FENTON, R.R. Dr BSc (Hons) Macq, PhD Macq Padstow Heights NSW (1985)

FERGUSSON, C.L. Dr BA (Hons) Macq, PhD NE. Wollongong NSW (1980)

FEWELL, M.P. Dr BSc (Hons), PhD ANU Armidale NSW (1988)

FINLAY, C.J. BSc Syd, North Ryde NSW (1975)

FOLDVARY, G.Z. BSc, MSc NSW Sydney NSW (1965)

FORD, G.W.K. MBE, MA Cantab, Jannali NSW (1974)

FROST, J.P. BA, DipEd, Quakers Hill NSW (1977)

GEORGE, C.R.P. St Ives NSW (1995)

GIBBONS, G.S. Dr MSc Syd, PhD NSW FAIG. Stanmore NSW (1966)

GILLESPIE, T.R. BSc Syd, Artarmon NSW (1986)

GLEN, R.A. Dr BSc(Hons) Syd, PhD Adel, St.Leonards NSW (1983)

GOLDRICK, R.B. Dr M.D. BS (Syd) F.R.A.C.P. Burradoo NSW (Assoc. 1998)

GOLDRICK, V.M. M.B., BS(Syd), DCH (Land.) Burradoo NSW (1998)

GOULD, R.E. Dr BSc, PhD Qld, Clayfield QLD (1973)

GOW, N.N. BSc (Hons) Ontario Canada (1966)

GRAHAM, I.T. Dr BAppSci(Hons) AppGeol NSW. Kingsford NSW (1987)

GRANT, A. Dr MBBS(Syd) BHA(NSW), DDR(Syd), FRACR McMahons Point NSW (1999)

GROVER, C. Belrose NSW (Assoc. 1991)

GROVER, OBE J.C. BE(Hons), MSc(Syd). Belrose NSW (1990)

GUY, B.B. Dr BSc, PhD(Syd). Bayview NSW (1968; P.2)

HADLEY, M. North Sydney NSW (1997)

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