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The Radium-Uranium Ratio
in Carnotites

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BY

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THE RADIUM-URANIUM RATIO IN CARNOTITES.

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INTRODUCTION.

One of the recent investigations undertaken by the Bureau of Mines, in pursuance of its endeavors to increase efficiency in the mining and treatment of the mineral resources in the United States, deals with methods of lessening waste in the extraction of radium from the carnotite and other uranium-bearing minerals of Colorado and Utah. In the course of this investigation it has been necessary to study the physical and chemical properties of these ores and to determine the radium and uranium content of many samples.

The radium-uranium ratio in different uranium minerals has been determined by various investigators, and among such minerals carnotite has naturally been included, though in rather surprisingly few instances. The general constancy of the ratios between the quantity of radium and that of uranium in most uranium minerals may be regarded as definitely established. The bearing of this experimentally demonstrated fact on the theory of the source of radium in a series of atomic disintegrations from the parent element uranium needs no comment.

Although the ratios so determined have been in the main constant and agree well in absolute value with what is to be expected theoretically from other radioactive measurements, still in some instances there have been rather large deviations and the explanations offered for these must be regarded as only partly satisfactory. The deviations have usually been in the direction of low ratios of radium to uranium, though deviations in the opposite direction have also been reported.

In so far as deviations from the normal radium-uranium ratio have been found for carnotite, these hitherto have been invariably low and the impression seems to have become rather general, particularly abroad, that carnotite, as a rule, contains anywhere from a few per cent to 30 per cent less radium than would correspond to its uranium content. It therefore became a matter of some theoretical interest to determine the ratio for a larger number of samples of carnotite than had been investigated.

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The determination of the ratio in carnotites has also practical value because of the increasing importance of carnotite as the largest known source of radium. The practice has been and is to buy and sell these ores on the basis of their percentage of uranium oxide (U_3O_8), although European buyers have sometimes insisted on making allowance for a supposed deficiency in radium. It is evidently of the greatest importance in determining what is the justification for such practice to know within what limits the radium content is fixed by the uranium content. With a view to determining these limits the investigation reported in this paper was undertaken.

WORK OF OTHER INVESTIGATORS.

For the first experimental demonstrations of the constancy of the radium-uranium ratio we are indebted to the work of Boltwood,[a] Rutherford,[b] Strutt,[c] McCoy,[d] and Eve.[e]

VARIATIONS OF RATIO IN MINERALS OTHER THAN PITCHBLENDE.

Later it began to be recognized that certain uranium minerals of secondary origin, of which autunite $[Ca(UO_2)_2(PO_4)_2.8H_2O]$ is one of the chief representatives, show a radium-uranium ratio below that of pitchblende. In 1909 Mlle. Gleditsch[f] announced that she had found a sample of French autunite showing only about 80 per cent of the normal (pitchblende) ratio. A low ratio for autunite was confirmed in 1910 by Russell,[g] who found, also in a sample of French autunite, a ratio only 27 per cent of the normal; while Soddy and Pirret[h] about the same time found that the ratio for a sample of Spanish autunite was 44.5 per cent of the pitchblende ratio.

To account for these low ratios in a sense consistent with the Rutherford and Soddy theory of radioactivity, two different explanations have been proposed. One assumes that the secondary minerals are too young for the quantity of radium to have accumulated to the maximum equilibrium value shown in older minerals such as pitchblende. The other explanation assumes that the secondary minerals,

[a] Boltwood, B. B., The origin of radium: Philos. Mag., vol. 9, 1905, pp. 599–613; On the ratio of radium to uranium in some minerals: Am. Jour. Sci., ser. 4, vol. 18, 1904, pp. 97–103; On the radioactivity of uranium minerals: Am. Jour. Sci., ser. 4, vol. 25, 1908, pp. 269–298.

[b] Rutherford, E. F., and Boltwood, B. B., The relative proportion of radium and uranium in radioactive minerals: Am. Jour. Sci., ser. 4, vol. 20, 1905, pp. 55–56; vol. 22, 1906, pp. 1–30.

[c] Strutt, R. J., On the radioactive minerals: Proc. Roy. Soc. London, ser. A, vol. 76, 1905, pp. 88–101; Note supplementary to paper, vol. 76, p. 312.

[d] McCoy, H. N., Ueber das Entstehen des Radiums: Ber. Deutsch. chem. Gesell., Jahrg. 37, Bd. 4, 1904, pp. 2641–2656; Radioactivity as an atomic property: Jour. Am. Chem. Soc., vol. 27, pt. 1, 1905, p. 391.

[e] Eve, A. S., The measurement of radium in minerals by the γ-radiation: Am. Jour. Sci., ser. 4, vol. 22, 1906, pp. 4–7.

[f] Gleditsch, Ellen, Sur le radium et l'uranium contenus dans les minéraux radioactifs: Compt. rend., t. 148, 1909, p. 1451; Sur le rapport entre l'uranium et le radium dans les minéraux radioactifs: t. 149, 1909, p. 267.

[g] Russell, A. S., The ratio between radium and uranium in minerals: Nature, vol. 84, 1910, pp. 238–239.

[h] Soddy, Frederick, and Pirret, Ruth, The ratio between radium and uranium in minerals: Philos. Mag., vol. 20, 1910, pp. 345–349; vol. 21, 1911, pp. 652–658.

because of a looser mechanical structure, are more easily leached by water and that radium is more readily removed than uranium, so that the ratio of radium to uranium is diminished by this process.

Additional evidence adduced principally by Marckwald and Russell [a] appears to support the leaching theory, for in autunite the ionium-uranium ratio was found to approach the theoretical value much more nearly than does the radium-uranium ratio, thus indicating a removal of radium, whereas lead, one of the end products of the uranium family, was found to be almost entirely lacking.

At the same time that Mlle. Gleditsch [b] announced the existence of a low radium-uranium ratio in autunite she reported a high ratio (about 16 per cent high) in thorianite from Ceylon. Explaining a high ratio appeared to present much more formidable difficulties than explaining low ones. Mlle. Gleditsch favored the view that either ionium or some unknown member between uranium and radium had a much longer period than was previously supposed, necessitating a greater lapse of time for the attainment of equilibrium. Consequently, according to this view, all the uranium minerals would be slowly advancing to an equilibrium content of radium higher than that in most pitchblendes.

The view held by Mlle. Gleditsch did not find general acceptance. Soddy and Pirret [c] had also examined autunite, pitchblende, and thorianite, and, although confirming a low ratio for autunite, as already stated, they failed to find a difference between the latter two exceeding 3 per cent, which they regarded as within their limits of experimental error.

In a later investigation extended to a much larger number of uranium minerals Mlle. Gleditsch [d] confirmed her earlier results, finding ratios of radium to uranium varying from 1.82×10^{-7} for chalcolite from Saxony to 3.74×10^{-7} for pitchblende from Cornwall; whereas for two pitchblendes from Norway she reported 3.48×10^{-7} and 3.64×10^{-7}, respectively.

CONSTANCY OF THE RATIO IN PITCHBLENDES.

The most recent experimental contribution to the subject is the searching examination by Heimann and Marckwald [e] of the radium-uranium ratio in eight samples of pitchblende from all the principal pitchblende localities of the world, including Joachimsthal, Saxony,

a Marckwald, W., and Russell, A. S., Über den Radiumgehalt einiger Uranerze: Ber. Deutsch. chem. Gesell., Jahrg. 44, Bd. 1, 1911, pp. 771–775; Über den Radiumgehalt von Uranerzen: Jahrb. Radioakt. Elektronik, Bd. 8, 1911, p. 457.

b Gleditsch, Ellen, loc. cit.

c Soddy, Frederic, and Pirret, Ruth, loc. cit.

d Gleditsch, Ellen, Sur le rapport entre l'uranium et le radium dans les minéraux actifs: Le Radium, t. 8, 1911, pp. 256–273.

e Heimann, Berta, and Marckwald, W., Über den Radiumgehalt von Pechblenden: Physik. Ztschr., Jahrg. 14, 1913, pp. 303–305; Jahrb. Radioakt. Elektronik, Bd. 10, 1913, p. 299.

German East Africa, Norway, Bohemia, Colorado, and Cornwall. Determinations were made by two entirely different methods—the emanation method and the gamma-ray method. For all eight samples the ratio was found to be constant within 0.4 per cent. The absolute value of the ratio was determined by comparison with a radium solution having its origin in the Hönigschmid[a] atomic-weight radium of the Institute for Radium Research in Vienna, and was found to be 3.328×10^{-7}. The satisfactory agreement of this number with the theoretical value of the ratio as calculated from radiation data [b] lend it additional reliability.

THE RATIO IN CARNOTITES.

As already stated, a few investigators have included carnotites among the uranium minerals they examined. The results of Boltwood[c] and of McCoy[d] show no abnormally low ratio for this mineral. Mlle. Gleditsch[e] reported for a sample of Colorado carnotite a ratio of only 2.34×10^{-7}, which corresponds to about 70 per cent of the normal ratio. Marckwald and Russell[f] found that the ratio was 91.6 per cent of normal ratio for a carnotite from Colorado and 71.5 per cent for one from Florida (?).[g] The impression seems to have been general, probably because of these results, that carnotite always has a low ratio.

By way of anticipation, the authors of this paper state here that with small samples they have sometimes confirmed the low ratios, finding one almost as low as that found by Mlle. Gleditsch, which, however, is to be regarded as exceptional. On the other hand, the authors have also found an equal number of high ratios (likewise in small samples only), some as high as the highest ratios found by Mlle. Gleditsch for any of the primary minerals and one considerably higher, 4.6×10^{-7}, which is the highest ratio yet reported for any uranium mineral.

What appears to the authors to be of the greatest significance is the fact that these abnormal ratios, both high and low, occur only in samples representing small quantities (a few pounds) of ore; whereas

[a] Hönigschmid, O., Revision des Atomgewichtes des Radiums und Herstellung von Radiumstandard-präparaten: Sitzb. K. Akad. Wiss., Abt. 2-a, Bd. 120, 1911, pp. 1617–1652.

[b] See calculation by Meyer, Stefan, Über die Lebensdauer von Uran und Radium: Sitzb. K. Akad Wiss., Abt. 2-a, Bd. 122, June, 1913, p. 1085.

[c] Boltwood, B. B., On the ratio of radium to uranium in some minerals: Am. Jour. Sci., ser. 4, vol. 18, 1904, pp. 97–103; On the radioactivity of uranium minerals: vol. 25, 1908, pp. 269–298.

[d] McCoy, H. N., Ueber das Entstehen des Radiums: Ber. Deutsch. chem. Gesell., Jahrg. 37, Bd. 3, 1904, pp. 2641–2656; Radioactivity as an atomic property: Jour. Am. Chem. Soc., vol. 27, pt. 1, 1905, p. 391.

[e] Gleditsch, Ellen, Sur le rapport entre l'uranium et le radium dans les minéraux actifs: Le Radium, t. 8, 1911, pp. 256–273.

[f] Marckwald, W., and Russell, A. S., Über den Radiumgehalt einiger Uranerze: Ber. Deutsch. chem. Gesell., Jahrg. 44, Bd 1, 1911, p. 771; Über den Radiumgehalt von Uranerzen: Jahrb. Radioakt. Elektronik, Bd. 8, 1911, p. 457.

[g] The authors of this paper have not been able to verify the occurrence of carnotite in Florida.

all samples from large lots (one ton to a carload) invariably show a ratio practically identical with that of pitchblende. This relation seems to suggest strongly a possible transposition of radium within the ore body rather than one of complete removal by leaching. The point is more fully discussed on a later page (pp. 26–27); but evidently there is no reason to suppose an abnormal ratio in carnotite provided the determination be made on a sample representative of a considerable portion of an ore body, whereas if the quantity of ore represented by the sample be small, the result may be either too high or too low.

DESCRIPTION OF SAMPLES.

The samples of carnotite investigated were chosen with the object of their representing the carnotite of all the principal localities in Colorado and Utah where the mineral has been found in important quantities. All grades of carnotite containing 1.5 to 33 per cent of U_3O_8 have been included.

The samples were not collected by the authors, nor were they taken with any reference to geological conditions or position in ore beds; they simply represent carnotites that come on the market either as specimens or in commercial quantities. As already mentioned, a special significance attaches to the specimens representing large quantities of ore. Owing to the large output of carnotite ore in 1913 the authors fortunately were able to obtain "pulp" samples representing large quantities of carefully sampled ore, which the authors believe to be of the utmost importance in obtaining the true content of radium. The samples analyzed were supplied through the courtesy of Messrs. W. L. Cummings, Thomas F. V. Curran, Gordon Kimball, W. L. Meyer, David Taylor, and the National Radium Institute.

DISCUSSION OF METHODS USED.

Two distinct determinations enter into the radium-uranium ratio which affect equally the accuracy of the result. The measurement of radium in carnotite, as in other ores, is most readily accomplished by the emanation method, which consists in the liberation by any suitable method of the radium emanation corresponding to the radium in the ore, the quantity of emanation and of radium being ascertained by using an electroscope with a gas-tight ionization chamber. The emanation method may be employed after the ore has been prepared by either of two methods: (a) The ore is kept in a closed vessel for a month or more until it has attained its maximum equilibrium quantity of emanation; or (b) the emanation is initially reduced to zero and subsequently allowed to accumulate in a closed vessel for a known period (usually several days), the maximum amount and

hence the radium content being then calculated by means of the Kolo-wrat tables.[a]   Only the former or "equilibrium" method was employed for final values in the radium determinations reported in this paper.   Results obtained by the accumulation method are reported on page 17 as being unsatisfactory.

Aluminum leaf electroscopes of the Wilson type, with ionization chamber and leaf system separate were used.   A full description of the electroscopes and the manipulative details will be found on subsequent pages.   The instruments were calibrated by means of analyzed pitchblende from Colorado, the ratio found by Heimann and Marckwald[b] of 3.328×10^{-7} being assumed to be correct.

The determination of uranium in carnotite presents especial difficulties because of the presence of vanadium, and many of the earlier proposed methods of separating the two metals have proved unsuitable.   A full description of the method used by Ledoux & Co., which the authors of this paper found satisfactory, is given on pages 21 and 22, as well as references to other methods that were sometimes employed for control.

The small quantity of uranium in most carnotites as compared with that in higher-grade ores renders difficult the attaining of the desired degree of accuracy in determining the uranium, and to a less degree the radium content.   The authors sought to overcome this difficulty by repeating determinations frequently and by employing additional methods of control in all cases of doubt.   All radium determinations have been checked by at least two independent methods of liberating the emanation.   The average results reported on pages 23 to 26 are believed to be accurate within 1 to 2 per cent.

THE EMANATING POWER OF CARNOTITE.

The term "emanating power" was first used by Boltwood[c] to signify the percentage loss of emanation from a radioactive substance, and in the determination of radium it was applied by him as an additive correction to the quantity of emanation liberated by direct solution. Such a correction is of especial importance in determining radium in carnotites in which the authors have found the emanating power to be high, from 16 to 50 per cent (see Table 1).   This high emanating power, which is one of the distinguishing characteristics of carnotite, was a controlling factor in the experimental procedure, hence it is discussed somewhat fully here.

a Kolowrat, Léon.   Le Radium, t. 6, 1909, p. 194.   Also given in most treatises on radioactivity.

b Heimann, Berta, and Markwald, W., Über den Radiumgehalt von Pechblenden: Physik. ztschr., Jahrg. 14, 1913, p. 303; Jahrb. Radioakt. Electronik, Bd. 10, 1913, p. 299.

c Boltwood, B. B., The origin of radium: Philos. Mag., vol. 9, 1905, pp. 599-613.

The loss of emanation by the ore is due to diffusion of the gas and is much lower (only 3 to 8 per cent) for dense, compact minerals like pitchblende than for carnotites, which have a looser mechanical structure. For a given sample the loss is doubtless, as suggested by Rutherford,[a] dependent on the degree of fineness to which the ore is pulverized. The authors of this paper have not undertaken any direct investigation of the relation between emanating power and fineness or any other property, but have ascertained that among different specimens fineness can not be the principal controlling factor, for there seems to be no relation whatever between the order of fineness of different samples and their emanating power.

Evidently a given percentage error in determining the emanating power to be used additively in obtaining the total emanation by Boltwood's method would more seriously affect the final result in the case of a carnotite than in that of an ore for which the relative value of the emanating power is small.

Repetition by the writers of this paper, of earlier determinations made by them, showed considerable variation in emanating power, which suggested that the emanation was not always removed to the same degree from the same sample. This variation is probably caused by differences in the volume of air passed over the ore, or to differences in pressure or velocity of the air, and the consequent drawing of varying amounts of emanation out of the more or less porous structure. As a remedy the authors used a simple modification of the Boltwood method, namely, making the determination of the emanating power and the emanation liberated by solution strictly "complementary" to each other—in the sense that each sample dissolved should represent part or all of the sample from which emanation had just been drawn to determine the emanating power. By this procedure it does not matter whether corresponding determinations of emanating power are concordant or not, so long as the sums obtained by adding corresponding determinations are in agreement. That this assumption is correct may be seen from the following table, which shows that for each ore the agreement for the total emanation is better than that of either of the individual values going to make up the sum. Only a few examples illustrative of this point are given because it was found more convenient to determine the total emanation in one operation, as described later. In this and other tables each ore is designated by the same number throughout.

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a Rutherford, E. E., Radioactive substances and their radiations, 1913, p. 364.

Table illustrating advantage of "complementary" emanation method.

Number of ore.	Emanating power, curies$\times$ 10^9.	Solution emanation, curies$\times$ 10^9.	Total[a] emanation per gram of ore, curies$\times$ 10^9.
2................	15.0 17.6	87.1 84.5	102.1 102.1
4................	14.0 11.7	58.6 60.8	72.6 72.5
5................	21.8 23.6	27.7 26.2	49.5 49.8
8................	4.38 4.45	8.93 8.50	13.3 13.0

[a] Each value in this column is the sum of the two values, on the same line, in the two preceding columns.

IMPRACTICABILITY OF SOLID-ORE RADIATION METHOD FOR CARNOTITE.

It should also be noted in discussing emanating power that the high and variable values exhibited by carnotite seem to preclude the possibility of employing for accurate determination any radiation method from the solid ore for either the alpha, the beta, or the gamma rays unless, in the employment of the gamma-ray method, a large quantity of ore could be kept for a month, and later measured, in an absolutely tight vessel.

EMANATION METHOD FOR THE DETERMINATION OF RADIUM.

For the liberation of emanation from carnotite the authors originally planned to use three methods: (a) Solution method—boiling in 1:1 HNO_3 solution; (b) fusion method—fusing with a mixture of Na_2CO_3 and K_2CO_3; (c) fusion and solution method—fusing with Na_2CO_3 and K_2CO_3, followed by solution in 5 per cent Na_2CO_3 solution, filtration, solution of the residue in 1:3 HNO_3 solution, and separate treatment of both solutions. The failure of methods b and c to give satisfactory results (see table on p. 17) led to the use of a fourth, (d) ignition method without flux. A description of the details of these methods is given in the following paragraphs.

SOLUTION METHOD.

The solution method may be used as described (p. 11) by adding the "emanating power" to the "solution emanation." In this procedure the authors found it advisable to modify the Boltwood method by making the two determinations complementary to each other, as already stated.

SOLUTION EMANATION METHOD IN A SINGLE OPERATION.

Unless one desires to know the emanating power itself it is simpler to determine the total emanation in one operation by sealing the ore in a very thin bulb, of the type shown in figure 1, for a month or more before breaking under acid to liberate the total emanation.

The bulb a, of 4 to 10 mm. diameter, according to the quantity of ore to be used, is blown very thin so as to break without endangering the outer flask f, contain-ing HNO_3. The ore is weighed into the bulb through b and then the glass stem c is sealed on and is constricted to make a complete seal at d, the upper end e being also sealed for convenience. The whole is introduced through a double-bored rubber stopper to a point just off the bottom of the flask f and may be broken by a slight downward rap on e. By boiling the acid, the ore is readily attacked and all of the emanation is boiled over into a gas burette (see fig. 2).
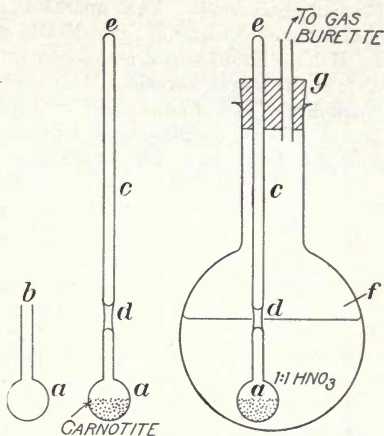
FIGURE 1.—Apparatus for determining emanation by sealed-tube method.

The results obtained with this method check excellently with the results of the "complementary" modified Boltwood method as can be seen from the following table:

Results of sealed bulb method for total emanation in one operation, compared with complementary method.

Number of ore.	Method used.	Emanating power, curies×10⁹.	Solution emanation, curies×10⁹.	Total emanation per gram of ore, curies×10⁹.
14........	{Sealed bulb........................... {Complementary.......................	3.906	7.188	11.09 11.09
15........	{Sealed bulb........................... {Complementary.......................	3.488	4.467	8.08 a 7.96
16........	{Sealed bulb........................... {Complementary.......................	3.191	3.916	7.08 a 7.11
18........	{Sealed bulb........................... {Complementary.......................	1.224	6.156	7.34 a 7.38
19........	{Sealed bulb........................... {Complementary.......................	2.993	5.606	8.54 a 8.60
20........	{Sealed bulb........................... {Complementary.......................	9.847	19.77	29.91 a 29.62
21........	{Sealed bulb........................... {Complementary.......................	10.72	13.12	23.61 a 23.84
22........	{Sealed bulb........................... {Complementary.......................	3.445	17.64	21.21 a 21.09

a Sum of results given, on same line, in the two preceding columns.

SOLUTION AND BOILING OFF EMANATION.

The method of solution and boiling off the emanation requires no especial explanation. The apparatus is shown in figure 2.

Hot water containing some NaOH is used in the gas burette k; 1:1 HNO_3 solution is used as a solvent of the carnotite. A glass stopcock at s is more convenient than rubber tubing and a clamp. All possibility of loss of emanation by the passage of water into the side arm t is avoided by allowing all air to pass up into k before the bulb a is broken. In case an ore is not sealed in glass, the same result may be accomplished by placing the ore in a filter paper and folding the paper so that it remains in the neck of the flask f until all air is expelled and the steam softens the paper, allowing it and its contents to drop into the acid. The stopcock should be closed at this time (or on breaking the glass bulb) and then gradually opened to prevent a sudden rush of gas from carrying undissolved ore up into the alkaline solution.

Pitchblende used for standardization purposes was treated in the same way as carnotite, either directly with correction for emanating power, or from a glass tube that had been sealed for one month.
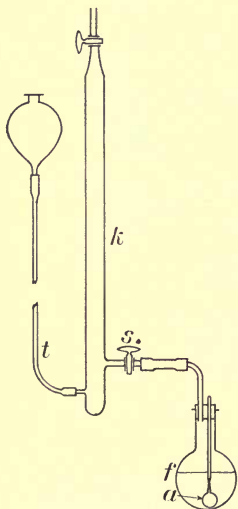
FIGURE 2.—Apparatus for dissolving carnotite and collecting the emanation.

FUSION METHOD.

The great advantage of "accumulation" over "equilibrium" emanation methods requiring a month, led the authors to attempt to employ a fusion method, since accumulation in solution is well known to give low results because of the removal of radium by precipitation or by adsorption. The method employed is as follows:

A quantity of ore sufficient to furnish enough emanation to produce a discharge of about one scale division per second, is thoroughly fused over a Meker burner in a platinum boat or dish with five or more times its weight of a mixture of one part Na_2CO_3 to one part K_2CO_3, enough time being allowed during fusion for all emanation to be driven off from the fused mass. The time of solidification is noted as the zero point for the accumulation of emanation and the fusion is set aside in a desiccator for three or four days; it is not necessary to keep the fused mass in a sealed vessel during accumulation, as a special experiment showed that there is no emanation loss from the

cold fusion. The second fusion to liberate emanation may be made either in the platinum boat in which the first was made by inserting the boat into a silica tube with ground glass joints as proposed by Ebler,[a] or better still, to attain a higher temperature the fusion is removed from the boat or dish and inserted into Jena combustion tubing of suitable diameter, in which it is held in place by glass wool plugs that, reacting with the flux, furnish a vigorous evolution of carbon dioxide to assist in the removal of emanation. The heating is accomplished by means of a Meker burner and is continued until the Jena glass completely collapses. A higher temperature is obtained in the bare Jena glass than in a platinum boat inside a silica tube, but on the other hand one loses the advantage of being able to repeat the fusion any number of times after renewed accumulation.

In spite of its great promise and actual success in experiments with pitchblende and crude sulphates, the fusion method has proved a failure for carnotite, even for high-grade ore requiring only a small quantity of flux, as will be seen in the table on page 17. If a higher temperature, by electric heating, were used the method might yield correct results, but such heating was not tried because of the same end being attained more readily by the method of ignition without flux. Two general precautions should be mentioned here: (1) The gases should be allowed to stand in a gas burette for about 10 minutes to permit the decay of thorium emanation before they pass into the emanation chamber. As no evidence has been obtained of the presence of thorium in carnotite this precaution may be omitted. (2) In case of a large evolution of carbon dioxide from the fusion in glass, a potash bulb should be inserted in front of the drying bulb to prevent carbon dioxide from entering the ionization chamber; otherwise, the fact that the "specific ionization" of carbon dioxide is greater than that of air makes the results obtained too high.

FUSION-AND-SOLUTION METHOD.

Fuse the ore with a mixture of Na_2CO_3 and K_2CO_3 as described for the fusion method, dissolve in a 5 per cent Na_2CO_3 solution, filter, dissolve the residue in $1:3$ HNO_3 solution, and remove the emanation from both the acid and alkaline solutions by passage of air for at least 10 minutes. Place each solution in a Jena flask and seal with a rubber stopper fitted with a glass tube having the upper end drawn out to a capillary point. After an accumulation period of several days the glass tube is connected with the collector by a piece of rubber tubing, and the point of the glass tube is broken inside the rubber tubing before boiling off the emanation, as described for solution method.

[a] Ebler, Erich. Über die Bestimmung des Radiums in Mineralien und Gesteinen: Ztschr. Elektrochem., Bd. 18, 1912, p. 532.

As shown by the table on page 17, the fusion-and-solution method gives results 10 to 20 per cent low, doubtless because of the adsorption of radium or radium emanation in the colloidal silica which almost invariably appears in the carbonate and sometimes in the acid solution also, even after refiltering once or twice. The method appears to give better results with substances containing little or no silica, but for those the simple direct-fusion method is also applicable. The carbonate solution usually filters very slowly, and on the whole the authors do not recommend the fusion-and solution method as being either accurate or convenient for carnotites.

IGNITION METHOD.

The application of the ignition method to carnotite was suggested by the ease with which the ore itself liberates its emanation even in

the cold, whereas the cold fusion loses none. Should such a difference persist at higher temperatures, ignition without flux would appear preferable. In fact, this method has been found entirely satisfactory.
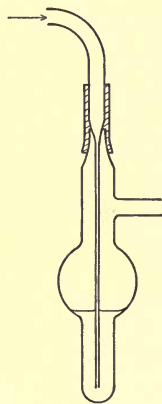
To hold the ore, straight pieces of Jena combustion tubing, about 4 to 10 mm. internal diameter, depending on the volume of the sample, and about 15 to 20 cm. long, were used. One end of a tube was drawn to a point and the weighed ore was introduced through the open end, which was then drawn out and sealed. Glass wool plugs were used to hold the ore in place in the middle of the tube. After standing one month or more the tube was connected by means of sulphuric-acid microdrying bulbs (fig. 3) to the exhausted electroscope on one side and to the outside air on the other side. After the capillary ends inside the rubber connections

FIGURE 3.—Sulphuric-acid microdrying bulb.

were broken air was allowed to pass over the ore into the electroscope, the tube being heated over a Meker burner $1\frac{1}{4}$ inches in diameter until the Jena glass completely collapsed. This treatment, as the following table shows, gives complete de-emanation.

Air was passed directly over the ore through a drying bulb into the electroscope—a procedure that is justified only when thorium is absent. That the ore contained no thorium is supported by two experimental observations—first, that the electroscope, after the radium emanation is pumped out, returns in a few hours to its normal natural leak, whereas it would not do so if contaminated by active deposit of thorium emanation; and, second, the results obtained by the ignition method agree well with those obtained by the solution method, in

which the emanation was always permitted to stand in a gas burette for 10 minutes before being passed into the emanation chamber. It seems certain, then, that there is little or no thorium in carnotites.

In the following table is a comparison of results obtained for a number of carnotite ores by using the four methods just described. Examination of these results shows that the solution method and the ignition method give concordant results, whereas the fusion method and the fusion-and-solution method give low results. For this reason the two latter methods were not employed in obtaining any of the data reported in Table I.

Comparison of results of different methods for de-emanating carnotites.

| Number of ore. | Total emanation in curies $\times 10^9$ by method of— | | | |
	Solution in 1:1 HNO_3.	Fusion with Na_2CO_3 and K_2CO_3.	Ignition.	Fusion and solution.
2	101.4	63.5	98.0	83.0
4	72.6		73.3	53.8
13	7.83	2.62	7.89	6.20
14	11.09		11.63	8.92
15	8.08			6.98
16	7.11		7.17	
17	8.66		8.65	7.38

ELECTROSCOPIC DETERMINATION OF RADIUM.

Two electroscopes were employed in making determinations, both being of the Wilson type, with sulphur insulation in the neck separating the ionization chamber from the leaf system. One of the electroscopes [a] had a chamber of 1 liter capacity. The other electroscope differed only in having a cylindrical ionization chamber of about ½-liter capacity.

This type of instrument has several advantages over that with the leaf system contained in the ionization chamber. The charging device is simpler and can always be brought back to a definite position, thus avoiding the danger of a variable electrical capacity. A charge can also be easily maintained for any desired time during the formation of induced activity, something that can not be conveniently done with instruments having a suspended charging rod controlled by a magnet.

ELECTROSCOPE WITH DETACHABLE IONIZATION CHAMBER.

A new type of electroscope has recently been devised by one of the authors to facilitate making a large number of radium determinations daily at a minimum expense for instruments.

[a] For a description and view of this electroscope see Moore, R. B., and Kithil, K. L., A preliminary report on uranium, radium, and vanadium: Bull. 70, Bureau of Mines, 1914, p. 66.

The new electroscope (fig. 4 and Pl. I, *A* and *B*) has an ionization chamber *a* (fig. 4), detachable from an upper cage *b*, containing the leaf system and microscope. By this device any number of ionization chambers may be used with one electroscope, thus avoiding duplication of the more expensive and delicate parts of the instrument. The advantages are obvious if one considers that in an ordinary emanation electroscope only one determination can be made daily, whereas in the detachable form as many may be made as one has ionization chambers. An ionization chamber costs about one-tenth as much as the complete instrument, hence an equipment equivalent in use to 10 electroscopes may be had for the cost of two.

FIGURE 4.—Cross section of electroscope with detachable ionization chamber (one-third size).

The ionization chamber may be of any form or size. For emanation determinations a cylinder of the type shown in figure 4 is recommended. A cylindrical electrode *e* is insulated from the chamber by means of the best quality of "bankers'" or "specie" sealing wax *d*, which also serves to make the vessel gas tight. The sealing wax is set in a brass collar that screws into the top of the ionization chamber onto a lead washer and can be readily removed when one desires to renew the insulation or examine its tightness. The electrode terminates outside the chamber in a small conical brass tip *c*, serving to make electrical contact with a spring *s*. When the upper part of the instrument is removed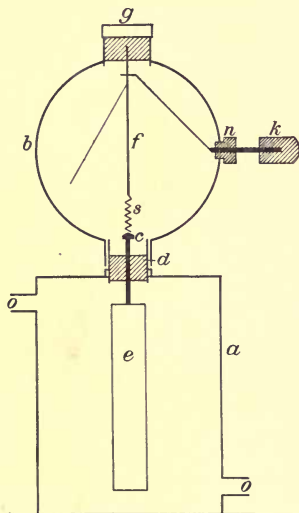 it is replaced with a friction cap of brass (Pl. I, *B*) to protect the electrode tip and sealing wax insulation from contamination. To the brass outlet tubes *o o* (fig. 4) glass stopcocks are attached by means of heavy rubber tubing securely wired on to insure a gas-tight joint. In all other respects the ionization chamber is similar to the older forms.

The upper part of the instrument consists of a cage *b* (fig. 4), of the usual form, housing the leaf system and, in this case, also acting as a support for the microscope. The leaf system *f* is suspended from the top of the cage instead of projecting up from the bottom. The rod to which the leaf is attached is set by means of sealing wax insulation into a brass cap *g*, which screws into the top of the cage from the outside and can be readily removed for the replacement of the
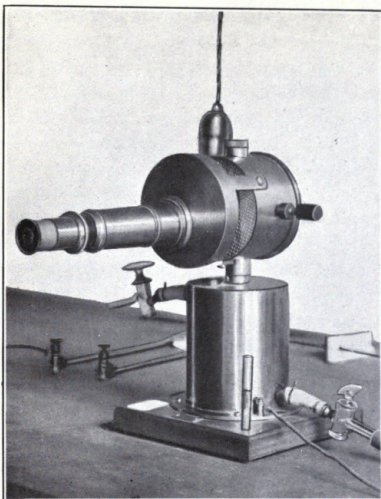
A. ELECTROSCOPE WITH INTERCHANGEABLE IONIZA-
TION CHAMBERS. THE ELECTRIC-LIGHT SOCKET AND
WIRE ABOVE THE INSTRUMENT ARE NOT PART OF IT.
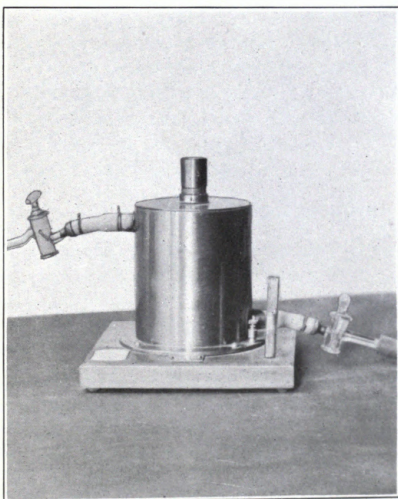
B. IONIZATION CHAMBER DETACHED FROM INSTRU-
MENT AND CAP IN PLACE.

aluminum leaf. If the cap shows any tendency to change position it should be set with a drop of solder to prevent disturbance of the calibration. At the bottom of the leaf support is a light brass spring s, serving to make electrical contact with the conical point c of the electrode of the ionization chamber. The spring should press lightly against the tip, enough to insure firm contact, but not so hard as to displace the leaf system from its normal position when the cage b is set down on the ionization chamber a.

One of the advantages of this electroscope is that the microscope, being attached directly and firmly to the leaf chamber (see Pl. I, A), can not become displaced relative to the leaf. The miscroscope is held in position by a heavy brass collar set in a vertical plate which is parallel to the front of the leaf chamber and is supported at a distance of about 1 inch from it by three supports screwed into the outside of the cage b (fig. 4).

The charging device k, of a simple and efficient type, is insulated from the cage by an ebonite plug n, which screws into the wall of the cage. The core of the plug is also threaded to accommodate the charging rod and to hold it firmly.

Other types of discharge chambers besides that for emanation may be employed, for example, an open chamber for solids, such as is used in the cursory examination of radioactive ores, or a large water chamber of the fontactometer type as used in determining the radioactivity of waters.

The purpose in designing this electroscope was to furnish a simple and inexpensive type of instrument, all the parts of which, except the microscope, can be made by any instrument maker or good mechanic. The design also permits of the replacement of any part without disturbing the rest of the electroscope. A detailed description of the instrument will be found in the May, 1915, issue of the Journal of Industrial and Engineering Chemistry.

STANDARDIZATION OF ELECTROSCOPES.

Standardization of electroscopes was carried out by dissolving about 40 milligrams of carefully analyzed pitchblende (see ore No. 12, p. 24) from Colorado in boiling $1:1$ HNO_3 solution according to the procedure described for carnotites on page 14. The radium content was assumed to be that corresponding to Heimann and Marckwald's [a] ratio of 3.328×10^{-7}. The pitchblende was analyzed by the method given for carnotite on page 21, omitting the procedure for the separation of vanadium. A number of shorter methods for determining uranium in pitchblende were found unreliable.

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[a] Heimann, Berta, and Marckwald, W., Über den Radiumgehalt von Pechblenden: Jahrb. Radioakt Electronik, Bd. 10, 1913, p. 299; Physik. Ztschr., Bd. 14, 1913, p. 303.

DATA FOR STANDARD PITCHBLENDE.

One gram of standard pitchblende contains 0.765 gram U_3O_8 or 0.649 gram U, and 2.16×10^{-7} gram of radium. The emanating power is 2.7 per cent. Therefore, 1 milligram dissolved directly gives $2.10 \times^{-10}$ curies of radium emanation.

CONTROL OF STANDARDIZATION.

A convenient and time-saving procedure for control of the standardization of electroscopes, after careful determinations and checking, was to measure the discharge produced by the penetrating radiation from about 1 milligram of radium, the element being in the form of bromide, in a small sealed glass tube. Another glass tube, large enough to accommodate the radium tube, was fixed in a vertical position in the wooden base of the electroscope at a distance such as to produce a discharge at the rate of about 1 division per second. This measurement was repeated every day, as was measurement of natural leak, before using the instrument. For variations of a few per cent attributable to fluctuations of temperature and atmospheric pressure, a correction was made. Greater variations were ascribed to changes in the leaf system necessitating recalibration, but recalibrating was not found necessary oftener than once in one to two months.

PROCEDURE IN USING THE ELECTROSCOPE.

After the natural leak had been determined and also the penetrating ray discharge as control of the calibration, the electroscope was evacuated to the desired degree, as determined by a mercury manometer attached to one of the stopcocks. After such evacuation either with an aspirator or a hand pump, the manometer was left connected with the electroscope for a few minutes to make sure that the electroscope was air-tight. A microdrying tube was then connected to one stopcock and the air containing emanation passed into the ionization chamber from the gas burette, the ignition tube, or the "emanating tube," as the case might be.

After standing about three hours the instrument was charged for about 10 to 15 minutes to the voltage used during measurement. It appeared to make little difference, probably because of the symmetrical form of the ionization chambers, whether induced activity was allowed to accumulate during the whole three hours in a chamber with or without charge. Therefore, the authors employed the method of charging for a short time immediately before measurement. Ten duplicate measurements were then made over a range of 40 scale divisions, from which the average rate of discharge was determined before correcting for the natural leak. The corrected rate of discharge

can be readily computed into terms of grams of radium by means of a standardization with pitchblende carried out in exactly the same manner as the measurement of the unknown sample of carnotite.

THE DETERMINATION OF URANIUM.

The method which proved most satisfactory for the determination of uranium in carnotite is the gravimetric one of Ledoux & Co., described by Moore and Kithil [a] and given below in full detail, including the volumetric determination of vanadium.

GRAVIMETRIC METHOD FOR VANADIUM AND URANIUM IN CARNOTITE.

Treat from 2 to 5 grams of ore, according to the proportion of vanadium, iron, and uranium present, in a covered beaker, with 10 c. c. of HCl and let it stand 15 minutes, shaking it occasionally. Add 5 c. c. of HNO_3 and heat on a steam bath. When quiet remove the cover and evaporate to dryness. Add 3 c. c. of HCl and 5 c. c. of water to the residue and let it stand on the steam bath for a few minutes, stirring occasionally. Dilute with 25 c. c. of hot water, filter into a small beaker, and wash the residue with warm water.

Some ores do not yield all the vanadium to this treatment; a little of it may remain with the insoluble residue. To make sure that all vanadium is in solution, ignite the residue in a platinum dish, treat it with 5 c. c. of HF and evaporate to dryness on a steam bath. Do not bake the residue. It is not necessary to expel all SiO_2. Add 3 c. c. of HCl to the residue from the HF treatment, and evaporate to dryness. Repeat this treatment to insure expulsion of HF. Treat residue with 2 c. c. of HCl and 2 c. c. of water and manipulate until any red crust is dissolved, then dilute the solution with water and filter it into the main liquid.

Pass H_2S into the liquid to separate copper, lead, and other metals of this group, filter and boil the liquid to expel the H_2S. Concentrate the liquid to 100 c. c., if necessary, and oxidize it with an excess of H_2O_2 and then neutralize with dry Na_2CO_3, adding 2 or 3 grams in excess. Boil the liquid for about 15 minutes until the yellowish uranium precipitate dissolves, leaving a brown precipitate which is principally iron. Filter and wash the iron precipitate with water, reserving the filtrate. Dissolve the iron precipitate in the least possible amount of HNO_3 (1:1) and add 10 c. c. of H_2O_2, neutralize with Na_2CO_3, add an excess of 2 grams of Na_2CO_3, and boil as before. Filter into the beaker containing the first filtrate. The iron precipitate may contain a little vanadium—reserve it for further treatment.

Evaporate the united filtrates from the iron precipitation to a volume of about 200 c. c., add 10 c. c. of strong HNO_3 and boil until all CO_2 is expelled. Neutralize the free acid with ammonia (until a slight permanent precipitate appears), then add 4 c. c. of HNO_3 for each 100 c. c. of liquid. Now add 10 c. c. of a 20 per cent lead acetate solution, and [enough (about 20 c. c.) of a strong solution of ammonium acetate to reduce the hydrogen ion concentration approximately to that of acetic acid.] The object is to precipitate the vanadium as lead vanadate in an acetic acid solution. The ammonium acetate solution may be made by mixing 80 c. c. of strong ammonia, 100 c. c. of water, and 70 c. c. of acetic acid 99 per cent pure.

Heat the liquid containing the lead-vanadate precipitate on the steam bath for one hour or more, filter on a tight filter, and wash with warm water. Dissolve the precipitate in the least possible quantity of hot, dilute [not stronger than 1:5] nitric acid,

[a] Moore, R. B., and Kithil, K. L., A preliminary report on uranium, radium, and vanadium: Bull. 70, Bureau of Mines, 1913, pp. 88–90.

neutralize as before, add 3 c. c. of HNO_3 in excess, add 2 c. c. of lead acetate solution, and repeat the precipitation of lead vanadate by adding ammonium acetate in excess, filter and add the filtrate to the one from the first precipitation of lead vanadate. Reserve the precipitate of lead vanadate for treatment as described below. Evaporate the united filtrates from the lead vanadate to about 400 c. c., add 10 c. c. of strong H_2SO_4 to separate the bulk of the lead (derived from the excess of lead acetate) as $PbSO_4$, filter, and wash the precipitate with cold water. Neutralize the filtrate from the $PbSO_4$ with ammonia and add freshly prepared $(NH_4)HS$ until the solution is yellow and the uranium and what little lead is present are precipitated as sulphides. Warm the mixture on a steam bath until the sulphides settle well. Filter and wash slightly with warm water.

Dissolve the precipitate in a No. 2 beaker with hot dilute (1:2) HNO_3, add 5 c. c. of H_2SO_4 and evaporate till fumes of H_2SO_4 appear, cool and take up with water, boil, and let the small precipitate of $PbSO_4$ settle until the solution is cold; filter, and wash the precipitate with [a little very] dilute H_2SO_4.

SEPARATION OF ALUMINA.

Nearly neutralize the filtrate with ammonia; have the solutions cool (not warmer than 30° C.), and add powdered carbonate of ammonia in about 2 grams excess to precipitate the aluminum, let the precipitate settle, filter, and wash with warm water. If the precipitate is bulky or is at all yellow, dissolve it in a little dilute H_2SO_4 and reprecipitate with ammonium carbonate as described above. Acidulate the filtrate from the alumina with H_2SO_4 and boil thoroughly to expel CO_2. Make the liquid slightly alkaline with NH_4OH while it is hot, and heat on the water bath until the ammonium uranate collects and settles. Filter and wash with very dilute (2 per cent) solution of NH_4NO_3. Do not allow the precipitate to run dry on the filter after the first washing. Dry the precipitate, ignite it in a porcelain crucible, and weigh as U_3O_8. Dissolve the precipitate in HNO_3 and test it with H_2O_2 for vanadium and with $(NH_4)_2CO_3$ for aluminum.

Dissolve the lead vanadate in dilute HNO_3, add 10 c. c. of H_2SO_4, and evaporate the mixture to fumes. Cool, take up with water [add fusion solution], add 10 c. c. of a concentrated solution of SO_2 to the mixture, boil until the excess of SO_2 is expelled and titrate the hot solution with a standard solution of potassium permanganate. The SO_2 reduces the vanadium in solution from V_2O_5 to V_2O_4. It is not necessary to filter out the lead sulphate before boiling to expel SO_2. The boiling is best done in a large flask. In expelling the excess of SO_2 it is necessary to boil the liquid for at least 10 minutes after the smell of SO_2 can no longer be detected.

The iron precipitate that was produced by the addition of Na_2CO_3 and H_2O_2 to the original acid solution may contain vanadium. Ignite the precipitate in a platinum crucible and fuse the residue with Na_2CO_3, leach the fusion with water, filter, and acidulate the filtrate with H_2SO_4. The filtrate may be addded to the main solution before reducing with SO_2, or reduced and titrated separately, as preferred.

For the details of other methods of control the reader is referred to Bulletin 70 [a]

In general it may be stated that the most prevalent errors in the determination of uranium result in the precipitation of some other oxide, such as SiO_2, Al_2O_3, or V_2O_3, along with uranium, which would produce a low radium-uranium ratio. To guard against errors from the presence of SiO_2 or Al_2O_3, the authors usually redissolved the U_3O_8

[a] Moore, R. B., and Kithil, K. L., A preliminary report on uranium, radium, and vanadium: Bull. 70, Bureau of Mines, 1914, pp. 82-91.

precipitate, passed the solution through a Jones's reductor, and determined the uranium volumetrically by titration with $KMnO_4$ solution.

RESULTS OF EXPERIMENTS.

The principal data in regard to the samples tested and the results obtained are given below. For convenience of reference each ore is designated by number, and the order of numbering is the same throughout this paper. Radium values representing the sum of two determinations were determined by the complementary method; those determined by the ignition method are so designated; all others were determined by the method of total emanation by solution in a single operation.

1. Sample of 65 pounds from Cripple Creek claim, Long Park, Paradox Valley, Colo. U_3O_8 content: 2.10; 2.08, and 2.12 per cent; average, 2.095 per cent; average U content, 1.78 per cent; average V_2O_5 content, 2.53 per cent. Ra per gram $\times 10^9$: 5.94, 6.11, and 5.99 (ignition method); average, 6.02×10^{-9} gram. Emanating power, 29.6 per cent. Ra/U = 3.38×10^{-7}.

2. Small sample from the Rajah claim, Roc Creek, Paradox Valley, Colo. U_3O_8 content: 33.19 and 33.24 per cent; average, 33.22 per cent. Average U content, 28.18 per cent; average V_2O_5 content, 14.05 per cent. Ra per gram $\times 10^8$: 1.50 + 8.71 = 10.21, 1.67 + 8.34 = 10.01, 1.76 + 8.44 = 10.20; average, 10.14×10^{-8} gram. Emanating power, 16.2 per cent. Ra/U = 3.59×10^{-7}.

3. Small sample from Black Fox claim, Bull Canon, south of Paradox Valley, Colo. U_3O_8 content: 1.63, 1.57, 1.60, and 1.58 per cent; average, 1.595 per cent. Average U content, 1.35 per cent; average V_2O_5 content, 5.22 per cent. Ra per gram $\times 10^9$: 2.15 + 2.06 = 4.21, 4.29, 4.30, 4.23 (ignition method); average, 4.26×10^{-9} gram. Emanating power, 50.5 per cent. Ra/U = 3.16×10^{-7}.

4. Small sample from Florence claim, Long Park, Paradox Valley, Colo. U_3O_8 content: 23.54 and 23.42 per cent; average, 23.48 per cent. Average U content, 19.92 per cent; average V_2O_5 content, 10.63 per cent. Ra per gram $\times 10^8$: 1.404 + 5.861 = 7.27; 1.166 + 6.082 = 7.25; 7.33 (ignition method); average, 7.28×10^{-8} gram. Emanating power, 17.7 per cent. Ra/U = 3.66×10^{-7}.

5. Small sample from a Curran claim, Long Park, Paradox Valley, Colo. U_3O_8 content: 24.03, 23.43, 24.75, and 24.37 per cent; average, 24.25 per cent. Average U content, 20.60 per cent; average V_2O_5 content, 13.51 per cent. Ra per gram $\times 10^8$: 2.18 + 2.77 = 4.95; 2.36 + 2.62 = 4.98; 4.95; 4.97 (ignition method); average, 4.96×10^{-8} gram. Emanating power, 45.8 per cent. Ra/U = 2.41×10^{-7}.

6. Small sample of a concentrate prepared by a method which may possibly have affected the Ra/U ratio. Hence the data for this sample are not included in Table I. U_3O_8 content: 9.20 and 9.05 per cent; average, 9.125 per cent. Average U content, 7.74 per cent; average V_2O_5 content, 10.08 per cent. Ra per gram $\times 10^8$: 2.166; 2.167; 2.184 (ignition method); average, 2.17×10^{-8} gram. Emanating power, 30.4 per cent. Ra/U = 2.80×10^{-7}.

7. Small sample from Florence claim, Long Park, Paradox Valley, Colo. U_3O_8 content: 3.16, 3.17, 3.23, and 3.19 per cent; average, 3.185 per cent. Average U content, 2.70 per cent; average V_2O_5 content, 4.82 per cent. Ra per gram $\times 10^9$: 4.26 + 6.35 = 10.61; 10.86; 10.58; 10.60; 10.94 (ignition method); average, 10.72×10^{-9} gram. Emanating power, 39.7 per cent. Ra/U = 3.97×10^{-7}.

8. Sample of 3,016 pounds from a Cummings claim, Bull Canyon, south of Paradox Valley, Colo. U_3O_8 content: 4.78, 4.72, 4.62, and 4.61 per cent; average, 4.68 per cent.

Average U content, 3.97 per cent; average V_2O_5 content, 4.10 per cent. Ra per gram $\times 10^9$: $4.38+8.93=13.31$; $4.45+8.50=12.95$; 12.42; 12.90 (ignition method); 13.67; average 13.05×10^{-9} gram. Emanating power, 33.9 per cent. $Ra/U=3.29\times10^{-7}$.

9. Sample of 29,118 pounds from same locality as No. 8. U_3O_8 content: 1.52, 1.57, and 1.48 per cent; average, 1.523 per cent. Average U content, 1.29 per cent; average V_2O_5 content, 4.00 per cent. Ra per gram$\times10^9$: $1.052+3.294=4.35$; $0.719+3.500=4.22$; 4.43; 4.41 (ignition method); average, 4.35×10^{-9} gram. Emanating power, 20.4 per cent. $Ra/U=3.42\times10^{-7}$.

10. Sample of about 4,000 pounds from same place as No. 5. U_3O_8 content: 2.31, 2.45, 2.35, and 2.48 per cent; average, 2.40 per cent. Average U content, 2.04 per cent; average V_2O_5 content, 5.27 per cent. Ra per gram$\times10^9$: 7.23; 7.40; 7.30 (ignition method); average, 7.31×10^{-9} gram. Emanating power, 29.0 per cent. $Ra/U=3.58\times10^{-7}$.

11. Small sample from Melrose claim, Green River district, Utah. U_3O_8 content: 4.14, 4.11, 4.12, and 4.16 per cent; average, 4.13 per cent. Average U content, 3.50 per cent; average V_2O_5 content, 5.07 per cent. Ra per gram$\times10^9$: $4.83+5.74=10.57$; $5.05+5.73=10.78$; 11.12; 10.87; 11.41 (ignition method); average 10.95×10^{-9} gram. Emanating power, 45.1 per cent. $Ra/U=3.13\times10^{-7}$.

[12. (Standard) pitchblende from Kirk mine, Gilpin County, Colo. U_3O_8 content: 76.40 and 76.58 per cent; average, 76.50 per cent. Average U content, 64.9 per cent. Ra per gram: 2.16×10^{-7} (calculated from Heimann and Marckwald's[a] Ra/U ratio of 3.328×10^{-7}). Emanating power 2.7 per cent, by two determinations of 5.98×10^{-9} and 5.73×10^{-9} curies, respectively.]

13. Sample of a carload lot (about 30 tons) from the claims of the Crucible Steel Co., Paradox Valley, Colo. U_3O_8 content: 2.74 and 2.82 per cent; average, 2.78 per cent. Average U content, 2.36 per cent; average V_2O_5 content, 4.67 per cent. Ra per gram$\times10^9$: $3.51+4.32=7.83$; 7.89 (ignition method); average, 7.86×10^{-9} gram. Emanating power, 44.7 per cent. $Ra/U=3.34\times10^{-7}$.

14. Sample of a carload lot (about 25 tons) from the same locality as No. 13. U_3O_8 content: 3.91 and 3.95 per cent; average, 3.93 per cent. Average U content, 3.33 per cent; average V_2O_5 content, 5.12 per cent. Ra per gram$\times10^9$: $3.90+7.19=11.09$; 11.09; average, 11.09×10^{-9} gram. Emanating power, 35.2 per cent. $Ra/U=3.33\times10^{-7}$.

15. Sample of a carload lot (about 20 tons) from same locality as No. 13. U_3O_8 content: 2.85 and 2.82 per cent; average, 2.835 per cent. Average U content, 2.41 per cent; average V_2O_5 content, 4.72 per cent. Ra per gram$\times10^9$: $3.488+4.467=7.955$; 8.076; average, 8.02×10^{-9} gram. Emanating power, 43.4 per cent. $Ra/U=3.33\times10^{-7}$.

16. Sample of a carload lot (about 22 tons) from same locality as No. 13. U_3O_8 content: 2.52 and 2.54 per cent; average, 2.53 per cent. Average U content, 2.16 per cent; average V_2O_5 content, 3.75 per cent. Ra per gram$\times10^9$: $3.191+3.916=7.107$; 7.077; 7.219 (ignition method); 7.174; average, 7.14×10^{-9} gram. Emanating power, 44.9 per cent. $Ra/U=3.32\times10^{-7}$.

17. Sample of a carload lot (about 19 tons) from same locality as No. 13. U_3O_8 content: 3.05, 3.03, and 3.06 per cent; average, 3.05 per cent. Average U content, 2.59 per cent; average V_2O_5 content, 4.66 per cent. Ra per gram$\times10^9$: 8.66; 8.65 (ignition method); average, 8.66×10^{-9} gram. Emanating power, 47.7 per cent. $Ra/U=3.34\times10^{-7}$.

18. Small sample from Kelly No. 3 lode, west of McIntyre district, Colorado, near Utah-Colorado boundary. U_3O_8 content: 25.63 and 25.71 per cent; average, 25.67 per cent. Average U content, 21.77 per cent; average V_2O_5 content, 22.3 per cent. Ra

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[a] Heimann, Berta, and Marckwald, W., Über den Radiumgehalt von Pechblenden: Jahrb. Radioakt. Elektronik, Bd. 10, 1913, p. 299; Physik. Ztschr., Bd. 14, 1913, p. 303.

per gram$\times 10^8$: $1.224+6.156=7.38$; 7.34; 7.37 (ignition method); average, 7.36×10^{-8} gram. Emanating power, 16.6 per cent. Ra/U$=3.38\times 10^{-7}$.

19. About 60 pounds of a composite sample of several ores. U_3O_8 content: 3.18, 3.26, 3.17, and 3.10 per cent; average, 3.18 per cent. Average U content, 2.70 per cent; average V_2O_5 content, 4.03 per cent. Ra per gram$\times 10^9$: 8.902 (ignition method); 8.935; average, 8.92×10^{-9} gram. Emanating power, 33.5 per cent. Ra/U$=3.30\times 10^{-7}$.

20. Small sample from Horse Mountain, Eagle County, Colo. U_3O_8 content: 7.81 and 7.75 per cent; average, 7.78 per cent. Average U content, 6.60 per cent; average V_2O_5 content, 8.80 per cent. Ra per gram$\times 10^9$: $9.85+19.77=29.62$; 29.91; 30.62; 30.98 (ignition method); average, 30.3×10^{-9} gram. Emanating power, 29.6 per cent. Ra/U$=4.59\times 10^{-7}$.

21. Small sample from a Meyer claim, South Park, Colo. U_3O_8 content: 9.52 and 9.20 per cent; average, 9.36 per cent. Average U content, 7.94 per cent; average V_2O_5 content, 3.85 per cent. Ra per gram$\times 10^8$: $1.07+1.31=2.38$; 2.36; 2.37 (ignition method); average, 2.37×10^{-8} gram. Emanating power, 45.2 per cent. Ra/U$=2.99\times 10^{-7}$.

22. A lot of several hundred pounds from the Wade and Taylor claims, Pac Creek, near Moab, Utah. U_3O_8 content, 7.52 per cent; U content, 6.38 per cent; average V_2O_5 content, 11.23 per cent. Ra per gram$\times 10^8$: $0.344+1.764=2.11$; 2.12; 2.15 (ignition method); average, 2.13×10^{-8}. Emanating power, 16.2 per cent. Ra/U$=3.34\times 10^{-7}$.

23. Sample of 1,120 pounds from the same locality as No. 22. U_3O_8 content, 11.62 per cent; U content, 9.86 per cent. Ra per gram$\times 10^8$: 3.29; 3.26 (ignition method); average, 3.28×10^{-8} gram. Emanating power, 25.1 per cent. Ra/U$=3.33\times 10^{-7}$.

24. Sample of about 1 ton of ore of unknown origin, very finely ground, possibly a mill product that had been mixed with a low-grade carnotite after the radium had been largely removed. U_3O_8 content: 8.83 and 8.85 per cent; average, 8.84 per cent. Average U content, 7.50 per cent; average V_2O_5 content, 6.87 per cent. Ra per gram$\times 10^9$: 3.99; 3.88; 4.24 (ignition method); average, 4.04×10^{-9} gram. Ra/U$=0.54\times 10^{-7}$.

The reasons for doubting this sample to be a natural carnotite ore are rather numerous. Its Ra/U ratio is abnormally low, and its origin could not be ascertained. Under the microscope it shows a network of crystalline needles partly soluble in water (apparently $CaSO_4$), such as could not have existed in the original ore, but must have formed after the ore was ground, because their length is several times the average diameter of other particles. On ignition considerable sulphur is distilled off, probably owing to reduction of sulphates by organic matter. For these reasons the authors do not believe it to be a natural carnotite, and have presented the data for whatever general interest they may have, without including them in Table 1.

A summary of the results obtained in the experiments with carnotite ores is presented in Table 1 following:

TABLE I.—*Results of experiments with carnotites.*

No. of ore.	Locality.	U_3O_8.	U.	Grams of radium $\times 10^9$ per gram of ore.	Emanating power.	Radium-uranium ratio. $\frac{Ra}{U} \times 10^7$.	Percentage of normal ratio (pitchblende ratio = 100 per cent).a
		Per ct.	Per ct.		Per cent.		
5	Long Park, Colo	24.25	20.6	49.6	45.8	2.41	72.4
21	South Park, Colo	9.36	7.94	23.7	45.2	2.99	89.8
11	Green River, Utah	4.13	3.50	10.95	45.1	3.13	94.0
3	Bull Canyon, Colo	1.60	1.35	4.26	50.5	3.16	94.9
8	Do	4.68	3.97	13.05	33.9	3.29	*98.8
19	(b)	3.18	2.70	8.92	33.5	3.30	99.1
16	Long Park, Colo	2.53	2.16	7.14	44.9	3.32	*99.7
14	Do	3.93	3.33	11.09	35.2	3.33	*100.0
15	Do	2.84	2.41	8.02	43.4	3.33	*100.0
23	Moab, Utah	11.62	9.86	32.8	25.1	3.33	*100.0
13	Long Park, Colo	2.78	2.36	7.86	44.7	3.34	*100.3
17	Do	3.05	2.59	8.66	47.7	3.34	*100.3
22	Moab, Utah	7.52	6.38	21.3	16.2	3.34	*100.3
18	McIntyre district, Colo	25.67	21.77	73.6	16.6	3.38	101.5
1	Long Park, Colo	2.10	1.78	6.02	29.6	3.38	101.5
9	Bull Canyon, Colo	1.52	1.29	4.35	20.4	3.42	*102.7
10	Long Park, Colo	2.40	2.04	7.31	29.0	3.58	*107.5
2	Paradox Valley, Colo	33.22	28.18	101.4	16.2	3.59	107.8
4	Long Park, Colo	23.48	19.92	72.8	17.7	3.66	109.9
7	Do	3.19	2.70	10.72	39.7	3.97	119.2
20	Eagle County, Colo	7.78	6.60	30.3	29.6	4.59	137.8
	Average						101.8

a In results preceded by an asterisk the sample represents a large quantity of ore (from several hundred pounds to 25 tons).

b Composite of several ores.

DISCUSSION OF RESULTS.

On inspecting the last two columns of Table I there appears to be only one possible conclusion as to the radium-uranium ratio of carnotite; namely, that it is identical with that of pitchblende in all large quantities of well-sampled ore. This appears to be true regardless of the locality of the deposit or the composition of the ore. The low and high ratios are found only in samples representing small quantities of ore, and the variations are apparently due to local transposition of radium within the ore bed; they are completely equalized on sampling sufficient quantities of ore. The authors are not prepared to go further into the nature of this transposition at the present time, because, as already stated, the samples were not collected with this object in view.

Of course, the fact that the average of all ratios in Table I should be within 2 per cent of the normal ratio is somewhat accidental; but that the average for all the large samples is within 1 per cent of the normal ratio appears by no means accidental, and seems to represent about the average of the limits of experimental error.

The question naturally presents itself as to whether high and low ratios for other minerals can be explained in the same way as for carnotite. As far as we are aware it is true that determinations of the radium-uranium ratio have been made, in all the minerals examined, on small samples only. On the other hand, it is to be recalled that high ratios had not been hitherto reported except for primary minerals, which are not affected as much by the action of water as secondary minerals are.

Furthermore, in the case of autunite, in which leaching certainly does produce very low ratios, no high ratios have ever been found to support the transposition theory as put forward for carnotite. In such instances it has been found that the leaching process removes the radium completely from association with the original uranium parent, disseminating it widely or, in exceptional cases, forming deposits containing considerable radium with no uranium, as found by Danne[a] in a specimen of pyromorphite from Issy L'Eveque.

The difference in the completeness of the removal of radium by leaching exhibited by autunite and carnotite may be due to the fact that the latter occurs in a region of very low rainfall; in fact, aridity seems to be a necessary condition for the existence of carnotite. Under such conditions and in view of the fact that the extent of many carnotite deposits is large, a transposition of radium might be expected rather than a complete removal.

The high degree to which carnotite gives up its emanation by diffusion as shown in Table 1 and discussed on pages 10 to 12, appears rather remarkable. The property does not seem to be connected with any other known properties of the ores and the authors are not able at present to do more than call attention to the fact, and also to note that carnotite appears to furnish in the solid state a more abundant source of radium emanation than any other mineral with the same radium content.

In conclusion it may be stated that from this investigation there seems to be no justification for regarding the radium-uranium ratio in commercial quantities of carnotite as being low or in any way abnormal. The practice of evaluating the ore from its uranium content appears to be correct within the limits of reliability of uranium determinations. In a later paper the authors expect to show that it will be more convenient as well as accurate to determine radium directly than to use the indirect method of a uranium analysis. It is, of course, needless to say that the latter procedure must always be the recourse when the genuineness of the product is uncertain or any other abnormality is suspected. However, in the case of a commercial quantity of correctly sampled carnotite, the uranium content

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a Danne, Jacques, Sur un nouveau minéral radifère: Compt. rend., t. 140, 1905, p. 241.

of which is accurately known, there remain no grounds whatsoever to suspect the radium content as being any less than in the proportion of 1 part of radium to 3,000,000 parts of metallic uranium.

SUMMARY.

1. Samples of carnotite representing large quantities of ore (a few hundred pounds to several tons) show a radium-uranium ratio identical with that of pitchblende (3.33×10^{-7}); this ratio is also in accord with the value calculated from radiation data.

2. Samples from small quantities of ore (hand specimens up to a few pounds) tend to exhibit abnormal ratios. In one instance the ratio was as low as 2.48×10^{-7}, and in another as high as 4.6×10^{-7}.

3. The most plausible explanation for these abnormal ratios seems to be that of transposition of radium within the ore bed, producing local differences which are equalized in large samples.

4. The "emanating power" of carnotite is high, and varies from 16 to 50 per cent.

5. In order to obtain concordant results by the Boltwood emanation method it was found desirable to determine the emanation liberated by solution in the same sample from which the emanating power had just been determined, thus making the two determinations strictly "complementary."

6. Radium may be easily determined in one operation by the emanation method, either by solution or by ignition from tubes in which it has been sealed for one month to reach equilibrium.

7. In contrast with the success of the solution and the ignition methods for de-emanating carnotite, the method of fusion with sodium and potassium carbonates and the fusion-and-solution method both gave low results and were abandoned.

ACKNOWLEDGMENT.

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