A strong solution of terbium nitrate gave an absorption spectrum consisting of one band in the blue as shown in the figure on preceding page.

The authors conclude from their results that there is only one terbium. By means of the bromate process, terbium is comparatively rapidly separated from gadolinium; and neodymium, if present, comes between the two. This work agrees with that of Urbain and not with that of von Welsbach.

DURHAM, N. H.

THE RADIUM : URANIUM RATIO IN CARNOTITES.[1]

By S. C. Lind and C. F. Whittemore.

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I. Introduction.

The constancy of the ratio of radium to uranium in the uranium minerals, and its significance in the theory of the origin of radium have been recognized for some time. For its experimental demonstration we are indebted to the early work of Boltwood,[2] Rutherford,[3] Strutt,[4] McCoy,[5] and Eve.[6]

At a somewhat later period 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 ratio below that of pitchblende. In 1909, Mlle. Gleditsch[7] announced that she had found a sample of French autunite showing only about 80% of the normal ratio. A low ratio was confirmed in 1910 by A. S. Russell,[8] who, also in a sample of French autunite, found only 27% of the normal ratio, while Soddy and Pirret,[9] about the same time, found a sample of Spanish autunite with 44.5% 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. The first supposes that the secondary minerals are too young for the quantity of radium to have accumulated to the maximum equilibrium value shown in the older minerals such as pitchblende. The second mode of explanation assumes that the secondary minerals, owing to a looser mechanical structure, are more subject to a *leaching process* by water and that radium is more readily removed than uranium, which results in a low ratio of the former to the latter.

[1] Published by permission of the Director of the Bureau of Mines.

[2] Boltwood, *Phil. Mag.*, **9**, 599 (1905); *Am. J. Sci.*, **18**, 97 (1904); **25**, 269 (1908).

[3] Rutherford and Boltwood, *Am. J. Sci.*, **20**, 55 (1905); **22**, 1 (1906).

[4] Strutt, *Proc. Roy. Soc. Lond.*, (*A*) **76**, 88 and 312 (1905).

[5] McCoy, *Ber.*, **37**, 2641 (1904); THIS JOURNAL, **27**, 391 (1905).

[6] Eve, *Am. J. Sci.*, **22**, 4 (1906).

[7] Mlle. Gleditsch, *Compt. rend.*, **148**, 1451; **149**, 267 (1909).

[8] A. S. Russell, *Nature*, **84**, 238 (1910).

[9] Soddy and Pirret, *Phil. Mag.*, **20**, 345 (1910); **21**, 652 (1911).

Additional evidence, adduced principally by Marckwald and Russell,[1] appears to support the "leaching" theory, since the ionium : uranium ratio was found much more nearly to approach theory in autunite than does the radium : uranium ratio, thus indicating a removal of radium, while lead, one of the end products of the uranium family, was found to be almost entirely lacking.

At the same time that Mlle. Gleditsch[2] announced the existence of a low radium : uranium ratio in autunite, she reported a high ratio (about 16% high) in thorianite of Ceylon. The explanation of a high ratio appeared to present much more formidable difficulties than the low ones. Mlle. Gleditsch favored the view that either ionium, or some other unknown member between uranium and radium, had a much longer period than previously supposed, necessitating a greater lapse of time for equilibrium to be attained. Consequently all the uranium minerals according to this view would be slowly advancing to an equilibrium quantity of radium higher than that in most pitchblendes.

This view of Mlle. Gleditsch's did not find general acceptance. Soddy and Pirret[2] had also examined autunite, pitchblende and thorianite; and while confirming a low ratio for autunite, as already stated, they failed to find a difference between the latter two exceeding 3%, 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[3] confirmed her earlier results, finding ratios of radium : uranium varying from 1.82×10^{-7} for chalcolite of Saxony, to 3.74×10^{-7} for pitchblende of Cornwall; while from two pitchblendes from Norway she reported 3.48×10^{-7} and 3.64×10^{-7}, respectively.

The most recent experimental contribution to this subject is the searching examination by Heimann and Marckwald[4] of the radium : uranium ratio in eight samples from all the principal pitchblende localities of the world, including Joachimsthal, Saxony, German East Africa, Norway, Bohemia, Colorado, and Cornwall. Determinations were made by two entirely different methods, the emanation method and the gamma-ray method. In all eight samples constancy of the radium : uranium ratio was found within 0.4%. The absolute value of the ratio was determined by comparison with a radium solution having its origin in the Hoenigschmid[5] 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

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[1] Marckwald and Russell, *Ber.*, **44**, 771–5 (1911); *Jahrb. d. Radioakt. u. Electronik*, 8, 457 (1911).

[2] *Loc. cit.*

[3] Mlle. Gleditsch, *Le Radium*, 8, 256 (1911).

[4] Heimann and Marckwald, *Jahrb. d. Radioakt. u. Elektronik*, **10**, 299 (1913); *Physik. Z.*, **14**, 303 (1913).

[5] Hoenigschmid, *Sitzb. Vienna Acad.*, *Abt. IIa*, **120** (Nov., 1911).

number with the theoretical value of the ratio as calculated from radiation data (see calculation by Stefan Meyer[1]) lends it a great degree of reliability.

Carnotites have been included among the specimens of uranium minerals examined by a few authors. From the results of Boltwood[2] and of McCoy,[2] no abnormally low ratio for this mineral was apparent, while Mlle. Gleditsch[2] reported, for a sample of Colorado carnotite, a ratio of only 2.34×10^{-7}, which corresponds to about 70% of normal ratio. Marckwald and Russell[2] found 91.6% of normal ratio for a carnotite of Colorado and 71.5% for one of Florida(?). From these results the impression seems to have been general that carnotite always has a *low* ratio.

The increasing importance of carnotite as one of the chief sources of radium has made it appear desirable to undertake a thorough examination of the radium : uranium ratio in a much larger number of samples of this mineral. To this end about twenty specimens of carnotite of all grades and from various localities have been examined. By way of anticipation, it may be stated here that, on *small* samples, we have confirmed in some cases the low ratios, finding one almost as low as that of Mlle. Gleditsch, which is to be regarded, however, as very exceptional. On the other hand, we have also found an equal number of *high* ratios (also in the case of 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 us to be of the greatest significance is the fact that these abnormal ratios, both high and low, occur only in samples representative of small quantities of ore (a few pounds), while all samples from large lots (1 ton up to a carload) invariably show a ratio practically identical with that of pitchblende. This appears to us to suggest strongly a theory of transposition within the ore bed rather than one of complete removal by leaching. This point will be more fully discussed in the Conclusion; but it is quite evident that there is no reason to suppose carnotite to be abnormal in ratio, provided the determination be made on a sample representative of a considerable portion of an ore bed, while rather large deviations in both directions are found by the examination of small samples.

II. Carnotite Samples.

The samples of carnotite investigated have been chosen with the object of representing the principal localities in Colorado and Utah where this ore has been found in any quantities of importance. All grades of carnotite from 1.5 to 33% 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 but are

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[1] Stefan Meyer, *Ibid.*, **122** (June, 1913).

[2] *Loc. cit.*

simply representative of carnotites as they come on the market either as specimens or in commercial quantities. As already mentioned, a special significance attaches to the specimens representative of large quantities of ore. Owing to the magnitude of the present production of carnotite ore we have been fortunate in obtaining ground samples representing large quantities of carefully sampled ore which we feel is of the utmost importance in obtaining correct values for radium content. We wish to take this opportunity of thanking all the gentlemen through whose courtesies we have been supplied with these samples.

III. General Discussion of Methods.

Two distinct determinations enter into the radium: uranium ratio which contribute equally to the accuracy of the result. The methods of determining radium in carnotite differ little from those employed for many other uranium ores and present no especial difficulties, provided suitable methods are used to liberate the emanation. We have employed the emanation method exclusively and always after attainment of equilibrium in the samples, sealed in glass tubes for a month or more; accumulation methods starting from zero emanation have not been used. Aluminium leaf electroscopes of the Wilson type were used with discharge chamber and leaf system separate. Calibration was made by means of analyzed pitchblende from Colorado assuming the ratio found by Heimann and Marckwald[1] of 3.328×10^{-7} to be correct.

The determination of uranium in carnotite does present, however, exceptional difficulties owing to the presence of vanadium, and many of the earlier proposed methods of separation have been found unsuitable. Full details of the method which we have found satisfactory are given in Section VII as well as references to other methods which we have employed in some cases for control.

The low uranium content of most carnotites as compared with other higher grade ores renders it difficult to attain the desired degree of accuracy in determining the uranium and, to a less extent, the radium content. We have sought to overcome this difficulty by repeating determinations frequently and by employing additional methods of control in all cases of doubt. These same precautions have also been used in the radium determinations, which have all been checked by two independent methods of liberating the radium emanation. Especial care has been taken in the case of all abnormal ratios to be sure that the deviations were real ones and not due to errors in the measurement either of radium or uranium. We believe that the average results reported in Sections VIII and IX are accurate to within 1–2%.

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[1] *Loc. cit.*

IV. The Emanating Power of Carnotite.

The term "emanating power" was used first by Boltwood[1] to signify the percentage loss of emanation from a radioactive ore, and was applied by him in the determination of radium as an additive correction to the quantity of emanation liberated by direct solution. The emanating power for many samples of carnotite has been found surprisingly large in the present investigation (compare Table IV, Col. 6) varying from 16 to 50%. This high degree of emanating power is not only to be noted as one of the distinguishing characteristics of carnotite but has also formed such a controlling factor in the experimental procedure that it deserves some preliminary attention.

The loss of emanation by the ore is due to a diffusion of the gas and is much lower (only 3 to 8%) in the case of dense, compact minerals like pitchblende than for carnotites which have a looser mechanical structure. For a given sample it is doubtless, as suggested by Rutherford,[2] dependent on the degree of fineness of the ore. We have not undertaken any direct investigation of the relation between emanating power and fineness, or any other property, but have ascertained that fineness cannot be the principal controlling factor among different specimens, as there is no relation whatever apparent 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 according to Boltwood, would more seriously influence the final result in case of a carnotite than in an ore where its relative value is small. Our earlier results showed on repetition considerable deviations in emanating power, which suggested that the emanation was not always removed to the same degree from the same sample. This is probably due to differences in the amount of air passed over the ore, or differences in air pressure or velocity, resulting in drawing varying amounts of emanation out of a more or less porous structure. A simple remedy suggested itself as a modification of the Boltwood method, namely, to make the determinations 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 the whole of the sample from which emanation had just been drawn to determine the emanating power. By this procedure it is indifferent whether various determinations of emanating power are concordant or not so long as the sums obtained by adding corresponding determinations are in agreement with each other. That the latter is in reality the case may be seen from Table I, in which it will be noted that, for each ore, the agreement for the total emanation is better than that of either of the in-

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[1] *Loc. cit.*

[2] Rutherford, "Radioactive Substances and Their Radiations," p. 364 (1913).

dividual values going to make up the sum. Only a few examples can be given in the table illustrative of this point, because it was soon found more convenient to determine the total emanation in one operation, as will be described below.

TABLE I.—ILLUSTRATING ADVANTAGE OF "COMPLEMENTARY" EMANATION METHOD.

Ore No.[1]	Eman. power in curies × 10^9.	+	Soln. eman. in curies × 10^9.	=	Total eman. in curies × 10^9 per 1 g. ore.
2	15.0		87.1		102.1
	17.6		84.5		102.1
4	14.0		58.6		72.6
	11.7		60.8		72.5
5	21.8		27.7		49.5
	23.6		26.2		49.8
8	4.38		8.93		13.3
	4.45		8.50		13.0

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 Fig. 1, for a month or more before breaking under acid to liberate the total emanation.

This method checks excellently with the "complementary" modified Boltwood method, as will be seen from Table II. 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*) containing HNO_3. The weighed ore is introduced into the bulb through (*b*) and then

TABLE II.—COMPARING RESULTS OF "SEALED BULB METHOD" (I) FOR TOTAL EMANATION IN ONE OPERATION, WITH "COMPLEMENTARY METHOD" (II).

Ore No.		Eman. power in curies × 10^9.	+	Soln. eman. in curies × 10^9.	=	Total eman. in curies × 10^9.
14	I	.....		.....		11.09
	II	3.906		7.188		11.09
15	I	.....		.....		8.08
	II	3.488		4.467		7.96
16	I	.....		.....		7.08
	II	3.191		3.916		7.11
18	I	.....		.....		7.34
	II	1.224		6.156		7.38
19	I	.....		.....		8.54
	II	2.993		5.606		8.60
20	I	.....		.....		29.91
	II	9.847		19.77		29.62
21	I	.....		.....		23.61
	II	10.72		13.12		23.84
22	I	.....		.....		21.21
	II	3.445		17.64		21.09

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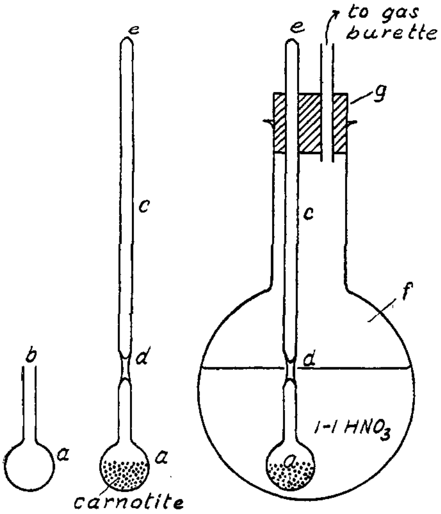
[1] This numbering of samples is the same as used throughout the paper. See Section VIII.

the glass stem (*c*) is sealed on and 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 (*g*) 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 buret (compare Fig. 11). The good agreement between this method and the one already described may be seen from Table II.

Fig. 1
Emanation Method
Using Sealed Tube



In connection with fusion methods to be later described, it was of interest to know the emanating power of the cold solidified mass resulting from the fusion of carnotite in sodium carbonate. On investigation its emanating power proved to be zero, which is in marked contrast with the action of carnotite in the cold without flux. Since we have always found (compare Table III) great difficulty in removing emanation even out of the hot fusion of carnotite in Na_2CO_3-K_2CO_3 mixture, although the same method works well on pitchblende or crude sulfates, the following suggested itself to us: If the cold fusion loses no emanation, while the ore alone loses large percentages, it seemed plausible that a direct ignition of the ore with no flux might bring about the liberation of emanation more readily than with a flux. This procedure proved eminently successful with carnotite (though a complete failure for crude sulfates) and has served in all cases as a control for the solution method.

Impracticability of Solid Radiation Methods for Carnotite.—It should also be noted while dealing with 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 alpha, beta, or gamma rays, unless, in the employment of the gamma-ray method, a large quantity of ore could be kept for a month and then measured in an absolutely tight vessel.

V. Emanation Method for the Determination of Radium.

For the liberation of emanation from carnotite we originally proposed to employ three methods: (1) Solution in boiling $1-1\ HNO_3$ (*a*) corrected for "emanating power" by the "complementary" method already described in Section IV; (*b*) by a single operation, by dissolving ore in equilibrium with emanation from a sealed tube. By reference to Table II it will be seen that both modifications of this method are equally suitable. (2) Fusion with a Na_2CO_3-K_2CO_3 mixture, which is later fused again in a Jena glass tube. This method will be seen from Table III to give very low results for carnotite and was soon abandoned. Perhaps by means of electrical heating to a higher temperature the emanation could be expelled from the fusion. The heating employed, both here and for the direct ignition method, was by means of a Méker burner. A Jena glass tube, into which the ore or fusion is introduced directly (without boat) and held in place by glass wool plugs, was held in the bare flame of this burner. (3) Direct ignition of the ore under conditions just described. This method was suggested by the high emanating power of carnotite and has proved entirely satisfactory, giving results which accord well with those of the solution method (cf. Table III).

In the solution method the emanation always was allowed to stand in a gas buret for ten minutes before passing into the electroscope, to allow any possible thorium emanation to decay; while in the ignition method air was passed directly over the heated ore through a small H_2SO_4 drying bulb into the exhausted electroscope. The fact that both methods give concordant results indicates the absence of thorium in carnotite. This is further supported by the return of the natural leaks of the electroscopes after a few hours to their original values, which would not be the case for the induced activity of thorium. (4) Fusion with Na_2CO_3-K_2CO_3 followed by solution in 5% Na_2CO_3, filtration, solution of the residue in 1-3HNO_3, and subsequent boiling off of both alkaline and acid solutions. This method, which is referred to as the *fusion and solution* method in Table III, will be seen to give results about 10–20% low. This we attribute to the almost invariable precipitation of some colloidal silica, involving the adsorption of radium and consequent loss of some emanation.

Of the four methods tried, two were found suitable and two unsuitable, as will be seen from the comparative results in Table III.

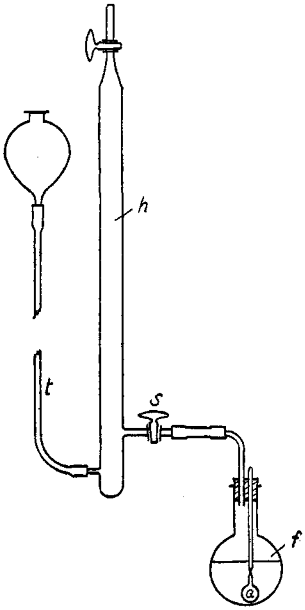
TABLE III.—COMPARATIVE RESULTS OF DIFFERENT METHODS FOR DE-EMANATING CARNOTITES.

	Total emanation in curies × 10^9 by method:			
Ore No.	(1) Solution in 1–1HNO_3.	(2) Fusion with Na_2-K_2CO_3.	(3) Ignition.	(4) 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

Solution and Boiling off the Emanation requires no especial explanation. The apparatus is shown in Fig. 11.

Hot water containing some NaOH is used in the gas buret (*h*); $1-1HNO_3$ is used as solvent in flask (*f*). A glass stopcock at (*s*) has been found 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 (*h*) before the bulb (*a*) is broken. In case of an ore not sealed in glass, the same may be accomplished by folding a filter paper containing ore, so that it remains in the neck of flask (*f*) until all air is expelled and the steam softens the paper, allowing it 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 alkali. 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 which had been sealed one month.

Fig 2
Apparatus for
Dissolving Carnotite
and
Collecting the Emanation



For the ignition method the ore was sealed in a straight piece of Jena combustion tubing drawn down to capillary points at both ends. The tubes were about 4 to 10 mm. internal diameter, depending upon the volume of the sample, and about 15 to 20 cm. long. The weighed ore was introduced through one end, which was then drawn out and sealed. The ore is held in place in the middle portion of the tube by means of glass wool plugs. After standing one month or more the tube was connected through H_2SO_4 micro-drying bulbs (cf. Fig. 2*a*) to the exhausted electroscope on one side and to the outside air on the other side. After breaking the capillary ends inside the rubber connections, air was allowed to sweep over the ore, the tube being heated by a Méker burner ($1\,^1/_{16}$ inch grating) until the Jena glass completely collapsed. This treatment will be seen, by reference to Table III, to give complete de-emanation.

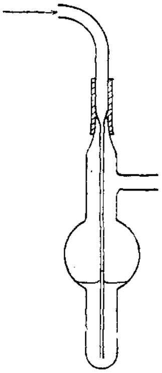
VI. The Electroscope Measurements.

Two electroscopes were employed, both of the Wilson type, with sulfur insulation between the leaf chamber and the ionization chamber below. The volumes of the latter were about 1 and $^1/_2$ liter, respectively, the former cubical and the latter cylindrical in shape.

Perhaps because of the symmetrical shape of the ionization chambers it appeared to make little difference whether equilibrium with induced activity was attained with or without a charge on the instrument. Consequently, after allowing the gas to remain in the electroscope for three hours, a charge was put on for 10 to 15 minutes before taking a series of ten readings over 40 scale divisions. Quantities of emanation were usually introduced such as to give a discharge of about 1 division per second.

Fig 2a

H_2SO_4 Micro-drying Tube



Standardization was carried out by dissolving about 40 mg. of carefully analyzed (cf. Sections VIII and XII) pitchblende of Colorado in boiling 1–1 HNO_3, assuming the Ra/U ratio as 3.328×10^{-7} according to Heimann and Marckwald.[1] The analysis of pitchblende was carried out by the method employed for carnotite (cf. Section VII), with the omission of the procedure for the separation of vanadium.

Data for Standard Pitchblende.—One gram of standard pitchblende contains 0.765 g. U_3O_8 = 0.649 g. U = 2.16×10^{-7} g. radium. Emanating power = 2.7%. Therefore, 1 mg. dissolved directly gives 2.10×10^{-10} curies of radium emanation.

As a control of standardization of the electroscopes, before each determination a gamma-ray measurement was carried out by placing a sealed glass tube, containing about 1 mg. of radium element in a tube fixed to the base of the discharge chamber, and measuring the rate of the discharge produced, which usually remained practically constant. Deviations of 2 to 3%, attributable to variations in pressure and temperature of the air, were used as direct corrections instead of the usual barometric and temperature corrections. Deviations greater than 2 or 3% were attributed to changes in the leaf system, necessitating recalibration. New calibrations were not found necessary oftener than in 1 to 2 months.

Emanation was introduced into the partially exhausted chamber through a micro-drying tube filled with H_2SO_4 (cf. Fig. 2*a*), any possible spray from which was prevented from entering the chamber by a short layer of cotton batting. After using the electroscope, the emanation was immediately removed by a current of dry air taken from outside the laboratory and the natural leak of the instrument determined the following day, before use.

VII. The Determination of Uranium.

The method which we have found most satisfactory for the determination of uranium in carnotite is a gravimetric one given below in full detail, including the volumetric determination of vanadium. Although having

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[1] *Loc. cit.*

no direct bearing on the present subject we include in Section VIII the data for vanadium in order to illustrate its occurrence in typical carnotites.

Gravimetric Method for Vanadium and Uranium in Carnotite[1] *and Other Ores.*—Treat from 2–5 g. of ore, according to the amount of V, Fe, and U present, in a covered beaker, with 10 cc. HCl and let it stand fifteen minutes with occasional shaking. Add 5 cc. HNO_3 and heat on a steam bath. When quiet, remove the cover and evaporate to dryness. Add 3 cc. HCl and 5 cc. H_2O to the residue and let it stand on the steam bath for a few minutes, stirring occasionally. Dilute with 25 cc. hot water, filter into a small beaker and wash the residue with warm water.

Some ores do not yield all the V to this treatment; a little of it may remain with the insoluble residue. To make sure that all V is in solution ignite the residue in a platinum dish, treat it with 5 cc. 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 cc. of HCl to the residue from the HF treatment, and evaporate to dryness. Repeat this treatment to insure expulsion of HF. Treat the residue with 2 cc. of HCl and 2 cc. H_2O and manipulate until any red crust is dissolved, dilute the solution with water and filter it into the main liquid.

Pass H_2S into the liquid to separate copper, etc., filter and boil the liquid to expel H_2S. Concentrate the liquid to 100 cc. if necessary, and oxidize it with an excess of H_2O_2 and then neutralize with dry Na_2CO_3, adding 2 or 3 g. in excess. Boil the liquid for about fifteen minutes, until the yellowish U 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 cc. of H_2O_2, neutralize with Na_2CO_3, add an excess of 2 g. and boil as before. Filter into the beaker containing the first filtrate. The iron precipitate may contain a little V—reserve it for further treatment.

Concentrate the united filtrates from the iron precipitation to a volume of about 200 cc., add 10 cc. 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 cc. of HNO_3 for each 100 cc. of liquid. Now add 10 cc. of a 20% lead acetate solution, and *enough* (about 20 cc.) 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 V as lead vanadate in an acetic acid solution. The ammonium acetate solution may be made by mixing 80 cc. of strong ammonia, 100 cc. of water and 70 cc. of 99% acetic acid.

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.

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[1] Cf. U. S. Bureau of Mines, *Bulletin* 70, by R. B. Moore and K. L. Kithil, p. 88.

Dissolve the precipitate in the least possible quantity of hot *dilute* (not stronger than 1-3) nitric acid, neutralize as before, add 3 cc. of HNO_3 in excess, add 2 cc. of lead acetate solution and repeat the precipitation of lead vanadate by adding ammonium acetate in excess, filter and add the *filtrate* to the first one. Reserve the precipitate of lead vanadate for treatment described below. Concentrate the united filtrates from the lead vanadate to about 400 cc., add 10 cc. of strong H_2SO_4 to separate the bulk of the lead (derived from the excess of lead acetate) as $PbSO_4$, filter it off and wash with cold H_2O. 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 separated as sulfides. Warm the mixture on a steam bath until the sulfides settle well. Filter and wash *slightly* with warm water.

Dissolve the ppt. with hot dilute nitric acid (1–2) and collect the solution in a No. 2 beaker, add 5 cc. of H_2SO_4 and evaporate to the appearance of fumes, cool and take up with water, boil and let the small amount of $PbSO_4$ settle until the solution is cold, filter it off and wash it with very little dilute H_2SO_4.

Separation of Alumina.—Nearly neutralize the filtrate with ammonia; have the solutions cool (not over 30°) and add powdered carbonate of ammonia in about 2 g. excess, let the precipitate of alumina settle, filter it off, wash with warm water and if it appears to be a considerable amount, or is at all yellow in color, dissolve it in a little dilute H_2SO_4 and reprecipitate with ammonium carbonate as above. Acidulate the filtrate from the alumina with H_2SO_4, 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 $(NH_4)NO_3$ (2%). Do not allow the precipitate to run dry on the filter after the first washing. Dry the precipitate and ignite it in porcelain, weighing 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 aluminium.

Dissolve the lead vanadate in dilute nitric acid, add 10 cc. of H_2SO_4 and evaporate the mixture until fumes appear. Cool, take up with water, and add fusion solution (see following paragraph), add 10 cc. of concentrated solution of SO_2 to the mixture, boil until the excess of SO_2 is expelled and titrate the hot solution with potassium permanganate solution. The reduction of the solution by SO_2 is from V_2O_5 to V_2O_4. It is not necessary to filter out the lead sulfate 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 ten minutes after the odor of SO_2 can no longer be detected.

The iron precipitate, which was produced by the addition of Na_2CO_3 and H_2O_2 to the original acid solution, may contain vanadium. Ignite it in a platinum crucible and fuse it with Na_2CO_3, leach the fusion with water, filter, acidulate the filtrate with H_2SO_4 and add it to the main solution before reducing with SO_2 or reduce and titrate it separately if preferred.

For the details of other methods of control one is referred to *Bulletin* 70, of the Bureau of Mines, 1913 and 1914, pp. 82 to 91.

In general, it may be stated that the most prevalent errors in the determination of uranium result in the precipitation of some other material, such as SiO_2, Al_2O_3, or V_2O_5, along with uranium, which would produce a low Ra/U ratio. To guard against the former two possibilities, we have usually redissolved U_3O_8 and passed the solution through a Jones' reductor to determine uranium volumetrically by titration with $KMnO_4$.

VIII. Experimental Data for Carnotites.

No. 1.[1] A sample from 65 lbs., Cripple Creek claim, Long Park, Paradox Valley, Colorado. Per cent. U_3O_8: 2.10, 2.08, 2.12; Av. *2.095* = *1.78%* U. Av. per cent. V_2O_5, 2.53. Ra per g. $\times 10^9$: 5.94;[2] 6.11; and 5.99 (ignition method). Av. 6.02×10^{-9} g. Em. power = 29.6%. Ra/U = 3.38×10^{-7}.

No. 2. A small sample from the "Rajah" claim, Roc Creek, Paradox Valley, Colorado. Per cent. U_3O_8: 33.19, 33.24; Av. *33.22* = *28.18%* U. Av. per cent. V_2O_5, 14.05. Ra per g. $\times 10^8$: 1.50 + 8.71 = 10.21; 1.67 + 8.34 = 10.01; 1.76 + 8.44 = 10.20; Av. 10.14×10^{-8} g. Em. power = 16.2%. Ra/U = 3.59×10^{-7}.

No. 3. A small sample from "Black Fox" claim, Bull Canon, south of Paradox Valley, Colorado. Per cent. U_3O_8: 1.63, 1.57, 1.60, 1.58; Av. *1.595* = *1.35%* U. Av. per cent. V_2O_5, 5.22. Ra per g. $\times 10^9$: 2.15 + 2.06 = 4.21, 4.29, 4.30, 4.23 (ignition); Av. 4.26×10^{-9} g. Em. power = 50.5%. Ra/U = 3.16×10^{-7}.

No. 4. A small sample from "Florence" claim, Long Park, Paradox Valley Colorado. Per cent. U_3O_8: 23.54, 23.42; Av. *23.48* = *19.92%* U. Av. per cent. V_2O_5, 10.63. Ra per g. $\times 10^8$: 1.404 + 5.861 = 7.27; 1.166 + 6.082 = 7.25; 7.33 (ignition). Av. 7.28×10^{-8} g. Em. power 17.7%. Ra/U = 3.66×10^{-7}.

No. 5. Small sample from a Curran claim, Long Park, Paradox Valley, Colorado. Per cent. U_3O_8: 24.03, 23.43, 24.75, 24.37; Av. *24.25* = *20.60%* U. Av. per cent. V_2O_5, 13.51. Ra per g. $\times 10^8$: 2.18 + 2.77 = 4.95; 2.36 + 2.62 = 4.98; 4.95, 4.97 (ignition); Av. 4.96×10^{-8} g. Em. power 45.8%. Ra/U = 2.41×10^{-7}.

No. 6. A small sample of a concentrate prepared by a method which may have affected its Ra/U ratio. Hence the data of No. 6 are not included in Table IV. Per cent. U_3O_8: 9.20, 9.05. Av. *9.125* = *7.74%* U. Av. per cent. V_2O_5, 10.08. Ra per g. $\times 10^8$: 2.166, 2.167; 2.184 (ignition); Av. 2.17×10^{-8} g. Em. power = 30.4%. Ra/U = 2.80×10^{-7}.

No. 7. Small sample from "Florence" claim, Long Park, Paradox Valley, Colorado. Per cent. U_3O_8: 3.16, 3.17, 3.23, 3.19; Av. *3.185* = *2.70%* U. Av. per cent. V_2O_5, 4.82. Ra per g. $\times 10^9$: 4.26 + 6.35 = 10.61, 10.86, 10.58 and 10.60; 10.94 (ignition); Av. 10.72×10^{-9} g. Em. power = 39.7%. Ra/U = 3.97×10^{-7}.

No. 8. Sample of 3,016 lbs. from a Cummings claim, Bull Canon, south of Paradox Valley, Colorado. Per cent. U_3O_8: 4.78, 4.72, 4.62, 4.61. Av. *4.68* = *3.97%*

[1] The order of numbering is one of convenience only, but the same numbers have been used for the same ores throughout the paper.

[2] Ra values consisting of the sum of two determinations refer to the "complementary" method; those without designation refer to method of total emanation by solution in one operation; ignition methods are designated as such.

U. Av. per cent. V_2O_5, 4.10. Ra per g. $\times 10^9$: 4.38 + 8.93 = 13.31; 4.45 + 8.50 = 12.95; 12.42, 12.90 (ignition), 13.67; Av. 13.05×10^{-9} g. Em. power = 33.9%. Ra/U = 3.29×10^{-7}.

No. **9.** Sample of 29,118 lbs. from same locality as No. 8. Per cent. U_3O_8: 1.52, 1.57, 1.48. Av. *1.523* = *1.29%* U. Av. per cent. V_2O_5, 4.00. Ra per g. $\times 10^9$: 1.052 + 3.294 = 4.35; 0.719 + 3.500 = 4.22, 4.43, 4.41 (ignition). Av. 4.35×10^{-9} g. Em. power = 20.4%. Ra/U = 3.42×10^{-7}.

No. **10.** Sample of about 4,000 lbs. from same location as No. 5. Per cent. U_3O_8: 2.45, 2.35, 2.48. Av. *2.40* = *2.04%* U. Av. per cent. V_2O_5, 5.27. Ra per g. $\times 10^9$: 7.23, 7.40, 7.30 (ignition). Av. 7.31×10^{-9} g. Em. power = 29.0%. Ra/U = 3.58×10^{-7}.

No. **11.** Small sample from Melrose claim, Green River District, Utah. Per cent. U_3O_8: 4.14, 4.11, 4.12, 4.16. Av. *4.13* = *3.50%* U. Av. per cent. V_2O_5, 5.07. Ra per g. $\times 10^9$: 4.83 + 5.74 = 10.57; 5.05 + 5.73 = 10.78, 11.12, 10.87; (ignition) 11.41. Av. 10.95×10^{-9} g. Em. power = 45.1%. Ra/U = 3.13×10^{-7}.

[No. **12.** (Standard) Pitchblende from Kirk Mine, Gilpin Co., Colorado. Per cent. U_3O_8: 76.40, 76.58. Av. *76.50* = *64.9%* U. Ra per g.: 2.16×10^{-7} (calculated from Heimann and Marckwald's[1] Ra/U ratio 3.328×10^{-7}, also in close agreement with a sample of analyzed pitchblende of known radium content from Boltwood). Em. power 2.7% by two determinations of 5.98 and 5.73×10^{-9} curies, respectively.]

No. **13.** Sample of a carload lot (ca. 30 tons) from the claims of the Crucible Steel Co., Long Park, Colorado. Per cent. U_3O_8: 2.74, 2.82. Av. *2.78* = *2.36%* U. Av. per cent. V_2O_5, 4.67. Ra per g. $\times 10^9$: 3.51 + 4.32 = 7.83; (ignition), 7.89. Av. 7.86×10^{-9} g. Em. power = 44.7%. Ra/U = 3.34×10^{-7}.

No. **14.** Sample of carload lot (ca. 25 tons) from the same locality as No. 13. Per cent. U_3O_8: 3.91, 3.95. Av. *3.93* = *3.33%* U. Av. per cent. V_2O_5, 5.12. Ra per g. $\times 10^9$: 3.90 + 7.19 = 11.09, 11.09. Av. 11.09×10^{-9} g. Em. power = 35.2%. Ra/U = 3.33×10^{-7}.

No. **15.** Sample of a carload lot (ca. 20 tons) from same locality as No. 13. Per cent. U_3O_8: 2.85, 2.82; Av. *2.835* = *2.41%* U. Av. per cent. V_2O_5, 4.72. Ra per g. $\times 10^9$: 3.488 + 4.467 = 7.955, 8.076; Av. 8.02×10^{-9} g. Em. power = 43.4%. Ra/U = 3.33×10^{-7}.

No. **16.** Sample of a carload lot (ca. 22 tons) from some locality as No. 13. Per cent. U_3O_8: 2.52, 2.54; Av. *2.53* = *2.16%* U. Av. per cent. V_2O_5, 3.75. Ra per g. $\times 10^9$: 3.191 + 3.916 = 7.107, 7.077 (ignition) 7.219, 7.174; Av. 7.14×10^{-9} g. Em. power = 44.9%. Ra/U = 3.32×10^{-7}.

No. **17.** Sample of a carload lot (ca. 19 tons) from same locality as No. 13. Per cent. U_3O_8: 3.05, 3.03, 3.06; Av. *3.05* = *2.59%* U. Av. per cent. V_2O_5, 4.66. Ra per g. $\times 10^9$: 8.66, 8.65 (ignition). Av. 8.66×10^{-9} g. Em. power = 47.7%. Ra/U = 3.34×10^{-7}.

No. **18.** Small sample from Kelly Lode No. 3, west of McIntyre District, Colorado, near Utah boundary. Per cent. U_3O_8: 25.63, 25.71; Av. *25.67* = *21.77%* U. Av. per cent. V_2O_5, 22.3. Ra per g. $\times 10^8$: 1.224 + 6.156 = 7.38, 7.34, 7.37 (ignition). Av. 7.36×10^{-8} g. Em. power = 16.6%. Ra/U = 3.38×10^{-7}.

No. **19.** About 60 lbs. of a composite sample of several ores. Per cent. U_3O_8: 3.18, 3.26, 3.17, 3.10; Av. *3.18* = *2.70%* U. Av. per cent. V_2O_5, 4.03. Ra per g. $\times 10^9$: (ignition) 8.902, 8.935; Av. 8.92×10^{-9} g. Em. power = 33.5%. Ra/U = 3.30×10^{-7}.

No. **20.** A small sample from Horse Mt., Eagle County, Colorado. Per cent. U_3O_8: 7.81, 7.75; Av. *7.78* = *6.60%* U. Av. per cent. V_2O_5, 8.80. Ra per g. $\times 10^9$:

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[1] *Loc. cit.*

9.85 + 19.77 = 29.62, 29.91, 30.62 (ignition) 30.98. Av. 30.3×10^{-9} g. Em. power = 29.6%. Ra/U = 4.59×10^{-7}.

No. **21.** A small sample from a Meyer's claim, South Park, Colorado. Per cent. U_3O_8: 9.52, 9.20; Av. *9.36* = *7.94*% U. Av. per cent. V_2O_5, 3.85. Ra per g. × 10^8: 1.07 + 1.31 = 2.38, 2.36, 2.37 (ignition). Av. 2.37×10^{-8} g. Em. power = 45.2%. Ra/U = 2.99×10^{-7}.

No. **22.** A lot of several hundred pounds from the Wade and Taylor claims, Pac Creek, near Moab, Utah. Per cent. U_3O_8: *7.52* = *6.38*% U. Av. per cent. V_2O_5, 11.23. Ra per g. × 10^8: 0.344 + 1.764 = 2.11, 2.12 (ignition) 2.15. Av. 2.13×10^{-8} g. Em. power = 16.2%. Ra/U = 3.34×10^{-7}.

No. **23.** Sample of 1,120 lbs. from the same locality as No. 22. Per cent. U_3O_8: *11.62* = *9.86*% U. Ra per g. × 10^8: 3.29, 3.26 (ignition). Av. 3.28×10^{-8} g. Em. power = 25.1%. Ra/U = 3.33×10^{-7}.

No. **24.** Sample of about one ton of ore of unknown origin, very finely ground, suspected of being a mill product from which radium had been largely removed, and mixed with a low grade carnotite. Per cent. U_3O_8: 8.83, 8.85. Av. *8.84* = *7.50*% U. Av. per cent. V_2O_5, 6.87. Ra per g. × 10^9: 3.99, 3.88, 4.24 (ignition). Av. 4.04×10^{-9} g. Ra/U = 0.54×10^{-7}.

NOTE.—The reasons for distrusting this sample as not being a natural carnotite ore are rather numerous. Its Ra/U ratio is very abnormally low, its origin could not

TABLE IV.—SUMMARY OF EXPERIMENTAL DATA FOR CARNOTITES.

Ore No.	Locality.[1]	% U_3O_8.	% U.	G. Ra. × 10^9 per 1 g. ore.	Emanating power in %.	Ra/U × 10^7.	% normal ratio (pitchblende = 100%).
5	Paradox Valley.....	24.25	20.6	49.6	45.8	2.41	72.4
21	South Park.........	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	South of Paradox....	1.60	1.35	4.26	50.5	3.16	94.9
8	South of Paradox....	4.68	3.97	13.05	33.9	3.29	98.8*
19	(A mixture)........	3.18	2.70	8.92	33.5	3.30	99.1
16	Long Park..........	2.53	2.16	7.14	44.9	3.32	99.7*
14	Long Park..........	3.93	3.33	11.09	35.2	3.33	100.0*
15	Long Park..........	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..........	2.78	2.36	7.86	44.7	3.34	100.3*
17	Long Park..........	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...	25.67	21.77	73.6	16.6	3.38	101.5
1	Long Park..........	2.10	1.78	6.02	29.6	3.38	101.5
9	South of Paradox....	1.52	1.29	4.35	20.4	3.42	102.7*
10	Paradox Valley.....	2.40	2.04	7.31	29.0	3.58	107.5*
2	Paradox Valley......	33.22	28.18	101.4	16.2	3.59	107.8
4	Long Park..........	23.48	19.92	72.8	17.7	3.66	109.9
7	Long Park..........	3.19	2.70	10.72	39.7	3.97	119.2
20	Eagle County.......	7.78	6.60	30.3	29.6	4.59	137.8
						Av.,	101.8

[1] In Colorado when not otherwise specified. See preceding sections for fuller details.

* All samples starred represent large quantities of ore (several hundred pounds up to 25 tons).

be ascertained. Examined under the microscope, it appears full of a net work of crystalline needles partly soluble in water (apparently $CaSO_4$), such as could not have existed in the original ore because the length of the crystals is several times the average diameter of other particles, showing that they must have formed after the ore was ground. On ignition, considerable quantities of sulfur are distilled off, probably owing to reduction of sulfates by organic matter. For these reasons we have not regarded it as natural carnotite, and have presented the data for whatever general interest they may have, without including them in Table IV, however.

IX. Discussion of Results.

On inspecting the last two columns of Table IV, 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, in general, to be true regardless of the locality or composition of the ore. The *low* and *high* ratios occur only in cases of small samples and are apparently due to local transposition of radium within the ore bed, resulting in differences which are completely equalized on sampling sufficient quantities of ore. We 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 IV should be within 2% of normal is somewhat accidental; but that the average of all the large samples is within 1% of normal appears by no means accidental and seems to represent about the average of our 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 the authors 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 in the case of primary minerals which are not so much subject to the action of water. Furthermore, in the case of autunite, where leaching certainly does produce very low ratios, no high ratios have ever been found to support the view of "transposition" 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, usually disseminating it very widely, or in exceptional cases forming deposits containing considerable radium with no uranium, as found by Jacques Danne[1] in a specimen of pyromorphite at Issy L'Eveque.

The difference in the completeness of 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

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[1] Jacques Danne, *Compt. rend.*, **140**, 241 (1905).

existence of carnotite. Under such conditions and in view of the fact that the extent of carnotite deposits is frequently quite 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 IV and discussed in Section IV, appears rather remarkable. This property does not seem to be connected with any other known properties of the ores and we are not able at present to do more than call attention to it, as well as 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.

X. Summary.

1. Samples of carnotite representing large quantities of ore (a few hundred pounds to several tons) show a Ra/U ratio identical with that of pitchblende, 3.33×10^{-7}.

2. Samples from small quantities (a few pounds) tend to exhibit abnormal Ra/U ratios. One instance as low as 2.48×10^{-7} and one as high as 4.6×10^{-7} have been found.

3. The most plausible explanation for these ratios seems to be one of "transposition" of radium within an ore bed, producing local differences which are equalized in mixing large quantities of ore.

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

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 more easily determined by the emanation method in one operation 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 successful solution or ignition method for de-emanating carnotite, fusion with carbonate, and also the fusion and solution methods both gave low results and were abandoned.

It gives us great pleasure to acknowledge our indebtedness to Professor R. B. Moore for his helpful advice during this investigation.

UNITED STATES BUREAU OF MINES.
DENVER, COLO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

CESIUM ALUM AND ITS PROPERTIES.

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Since the discovery of cesium by Bunsen, in 1860, its compounds have been investigated at various times, but a broad field for research still