tion of nitric oxide was produced from nitrogen and carbon dioxide as was produced from air.

3. The effect of reduced pressure upon the equilibrium obtained was very slight.
4. The results obtained show that the concentration of nitric oxide produced from carbon dioxide–nitrogen mixtures was increased by 30–40% when the current was increased by 50%.
5. The results obtained show that the reaction between nitrogen and carbon dioxide holds little promise as a means of fixing nitrogen by the arc process.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

THE ORIGIN OF PROTOACTINIUM

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The major part of this investigation grew out of work started several years ago to separate protoactinium from America's most important uranium ore, carnotite. As expected, after much preliminary work, the presence of protoactinium was established. From the standpoint of radioactivity, it is generally considered as being the parent of actinium and hence takes its place at the head of the actinium series. The fact has long been established that the radioactive elements allow themselves to be arranged in three great divisions, the uranium, the thorium and the actinium series. The exact relation of the actinium series to the uranium and thorium series of radioactive elements is as yet not definitely known. This investigation was undertaken with the hope of throwing some light on this very important relationship.

The uranium disintegration series, as it is now generally represented, shows the actinium series as springing from uranium II, by the way of uranium Y, although it is generally indicated that this is uncertain.[1] According to this scheme, the actinium series is formed in a dual α-ray change from uranium II, the remainder of the uranium II atoms forming the ionium–radium series. At present the most widely accepted percentages for the numbers of uranium atoms forming the ionium–radium and actinium series are ninety-seven and three per cent., respectively. Obviously, if a definite percentage of the uranium atoms disintegrates to form the actinium series, the ratio between this series, or any member of it, to uranium, should be a constant in uranium bearing minerals, just as the radium–uranium ratio is constant.

[1] Meyer and Schweidler, "Radioaktivität," **1927**, p. 347; also Kohlrausch, "Radioaktivität," **1928**, p. 8.

If, on the other hand, protoactinium exists in a series independent of uranium, the protoactinium–uranium ratio should show some variation in different minerals used as sources of protoactinium. While it is true that the proportion of the isotopes of stable elements, such as chlorine, is relatively constant in nature, it does not follow that constancy of proportion holds for radioactive isotopes, since their disintegration constants are generally quite different.

Boltwood[2] showed that the actinium content of minerals is roughly proportional to their uranium content. Fussler[3] measured the same relation for three different samples of carnotite and obtained values that are in the ratio 1.261 : 1.644 : 1.00. Meyer and Hess[4] made similar determinations on different uranium minerals and came to the conclusion that the actinium–uranium ratio is constant. Others[5] have made similar determinations on the uranium Y–uranium and the actinium series–uranium relations and report values ranging all the way from two to five per cent. When the results of all these investigations concerning this ratio are compared, the degree of variation is so marked that we cannot, even today, say with certainty that the ratio between the actinium series, or any member of it, and uranium, is constant.

The results of this investigation indicate that the protoactinium–uranium ratio is far from constant, and consequently strengthens the view advocated in recent years by several investigators that the actinium series is not a direct offspring of the uranium series. This conclusion is based upon the quantitative determination of the protoactinium–uranium ratio of different uranium minerals from widely separated localities. A rich carnotite from Colorado, two pitchblendes from Bohemia, a soddite from the Belgian Congo, and a thorianite from Ceylon, were analyzed for their protoactinium and uranium contents.

Preliminary Work.—First a method had to be developed for the quantitative separation and recovery of tantalum from carnotite, since tantalum is the nearest homolog of protoactinium and must be added to protect the minute quantities of protoactinium to be extracted. After obtaining confidence in the technique involved, an extensive amount of work still remained to be done on simplifying and standardizing a method, applicable not only to carnotite but, with little modification, to other uranium minerals as well.

In attacking a problem of this sort one naturally begins with methods which earlier investigators have followed in extracting protoactinium from uranium minerals. Hahn and Meitner[6] in their extended study of proto-

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[2] Boltwood, *Am. J. Sci.*, [4] **25**, 269–298 (1908).

[3] Fussler, *Phys. Rev.* [2] **9**, 142–147 (1917).

[4] Meyer and Hess, *Sitzb. Wien. Akad.*, **128**, 2a, 909–924 (1919).

[5] Kohlrausch, "Radioaktivität," **1928**, p. 757.

[6] Hahn and Meitner, *Ber.*, **52**, 1812–1828 (1919).

actinium, confined themselves to pitchblende as a source of the element. They used three different methods of extraction: (1) decomposition of the ore with sodium bisulfate, which leaves the protoactinium in the insoluble residue; (2) treatment with fifty per cent. hydrofluoric acid plus sulfuric acid, which puts the protoactinium into solution; and (3) the nitric acid treatment, which leaves most of the protoactinium in the insoluble residue.

For the preliminary work of separating protoactinium from carnotite the bisulfate method of Hahn and Meitner seemed best adapted because, in their hands, better results were more readily obtained by it than with the other two methods.

The bisulfate method is, briefly, as follows: A few milligrams of tantalic oxide is added to the sample of mineral and the whole thoroughly fused with sodium bisulfate. The fused mass is then thoroughly lixiviated with boiling water, to which sulfur dioxide is added to aid in the quantitative precipitation of the tantalum. Upon filtering, radium, radio-lead, tantalum, protoactinium and small quantities of radium E, polonium, ionium and uranium X remain in the residue and uranium, ionium plus uranium X, actinium, radium E and polonium in the filtrate. The residue is now ignited in a porcelain crucible and then transferred to a platinum dish. Hydrofluoric acid, a few drops of sulfuric acid and a few drops of thorium nitrate solution are now added and the solution warmed on a water-bath. The tantalum and protoactinium are brought into solution in from one to two hours. Filtering through a paraffined funnel leaves radium, radio-lead, and traces of ionium plus uranium X in the residue, and tantalum, protoactinium and traces of radium E and polonium in the filtrate. The filtrate is now brought to the fuming point of the sulfuric acid and the residue treated with aqua regia to remove the last traces of radioactive impurities. The insoluble material left after the aqua regia treatment consists of the oxides of tantalum and protoactinium.

Hahn and Meitner refer to the fact that they had great difficulty in removing the tantalum from the platinum dish after bringing the solution to the fuming point of sulfuric acid, just before the aqua regia treatment. They solved the problem by adding a small quantity of an iron salt to the solution just before bringing it to the fuming point. This put the residue in a form less difficult to remove from the dish. The writer found that the tantalum, in the absence of an iron salt, is not only difficult to remove, but tends to form a glaze, especially around the side of the dish, which because of its transparency makes most of the residue invisible; but if water is added at this point and the surface of the dish carefully rubbed with a horn spatula, the glaze of tantalum comes off and forms a white suspension of tantalic acid. With a little patience all of the tantalum may be removed from the dish without the addition of an iron salt. In some cases as high as ninety-five per cent. of the tantalum was recovered from the pitchblende samples in this way.

Carnotite.—Carnotite is a potassium urano vanadate and even high grade material is very rich in silica. Consequently it was found very difficult to apply this method satisfactorily, for when the bisulfate fusion is made, the tantalum remains with the silica in the insoluble residue. After sufficient hydrofluoric acid had been added to remove all of the silica and put the tantalum in solution, nothing like quantitative returns could be made on the tantalum, because a considerable quantity of the tantalum is volatilized in the hydrofluoric acid treatment.[7] It was found in later experiments with other minerals, where much less silica was involved and hence much less hydrofluoric acid used, that the recovery on tantalum increased. However, the tantalum recovered from the carnotite by this method showed an increase in activity characteristic of protoactinium.

In the earlier experiments the recovered tantalum was badly contaminated with radium, which persisted very strongly. The barium in the carnotite remained in the insoluble residue, and a relatively large amount of it would be carried through with the hydrofluoric acid, since barium fluoride is far more soluble than barium sulfate.

Tantalum can be freed from radium by a procedure based on two findings: one is that freshly precipitated tantalic acid is very soluble in very dilute hydrofluoric acid, and the other is that tantalum is readily precipitated, even from solutions of hydrofluoric acid, by means of ammonium hydroxide.[8] The writer found that quantitative recoveries could be made in this way, especially in the presence of the small amount of hydrofluoric acid used in these separations. The mineral sample, to which the tantalic oxide had been added, was fused as before, boiled in a large excess of water and the solution filtered through a paraffined funnel. A beaker containing ammonium hydroxide was placed under it and some very dilute hydrofluoric acid poured through the precipitate. The tantalum, some silica and perhaps a little barium fluoride were carried through into the ammonium hydroxide. The tantalum immediately precipitated, and if much silica is present, it is precipitated at this point. Under any condition, much of the silica is carried into the filtrate, and the amount of hydrofluoric acid necessary to remove it will cause the yield of tantalum to be low. The operation of dissolving the tantalic acid from the residue on the filter paper with dilute hydrofluoric acid and precipitating it with ammonium hydroxide must, therefore, be repeated several times. This procedure has the advantage of not precipitating any of the barium and

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[7] Travers, *Compt. rend.*, **166**, 494 (1918).

[8] Hopkins, "Chemistry of the Rarer Elements," D. C. Heath and Co., **1923**, p. 235.

radium along with the tantalum, because ammonium hydroxide will not precipitate barium from dilute solutions of barium salts.

By several repetitions of the above operation, the tantalum precipitate is completely freed from traces of barium and radium salts. The tantalum precipitate is finally filtered, washed and ignited. Traces of silica are removed with hydrofluoric acid. For final purification, and to give the precipitate a good texture, it is fused with potassium bisulfate and the melt dissolved in boiling water. After filtering, washing and igniting, the tantalic oxide comes out as a fine, white powder which is easily brushed from the crucible.

With these modifications, the recoveries from carnotite were much better than those obtained by the Hahn and Meitner method, and the separations, in the main, less difficult to carry out. Even with all of the above precautions, it is difficult to remove the last traces of radium. This was verified time and time again during the course of this investigation. Since the amount of protoactinium is determined by the activities of these tantalum preparations, it is very important to rid them entirely of other active material. Because of the generally low recoveries made on the tantalum by fusion with bisulfate, it was reluctantly abandoned.

The procedure finally employed for the extraction of protoactinium from carnotite was developed from a method used by Russell and Widdowson[9] for the extraction of protoactinium from pitchblende. By introducing some modifications, the Russell and Widdowson method can be applied not only to carnotite, but to other uranium minerals as well. Their method is, briefly, as follows. The mineral sample is boiled vigorously for an hour in dilute nitric acid and then filtered. The residue is active. A few milligrams of tantalic oxide is added to this residue and the whole mass fused with potassium hydroxide in a nickel crucible. The melt is dissolved in cold water and the residue, which is inactive, is filtered out. The alkaline solution is now added to the nitric acid solution, then a few cubic centimeters of dilute sulfuric acid and the solution is neutralized with ammonium hydroxide. Upon boiling, the tantalum separates out as a flaky precipitate. The precipitate is filtered out, washed, and then fused with potassium bisulfate to remove elements other than those of atomic number ninety-one. Naturally, some modification must be made here for minerals such as carnotite, which contains considerable barium, and at the same time have a high silica content.

In this procedure the silica is all changed to the soluble silicate in the potassium hydroxide fusion and then when the alkaline solution is added to the nitric acid solution, great quantities of silicic acid are precipitated, from which it is very difficult to separate the small amount of tantalum. In fact, it is almost impossible to separate quantitatively the small amounts of tantalum, if there is much silica present.

[9] Russell and Widdowson, *Phil. Mag.*, **46**, 925 (1923).

It was found in the course of this work, that in order to get quantitative returns on the tantalum, it was necessary to add ammonium hydroxide until a small amount of the uranium, and perhaps a little vanadium, were precipitated along with the tantalum. The uranium and vanadium were removed later. As to final fusion with bisulfate, carnotite presents a problem because of the presence of barium. It is obvious that barium cannot be removed by fusion with bisulfate.

In order to utilize the fusion with potassium hydroxide for the extraction of tantalum from carnotite, it is evident from all the preceding work that most of the silica must be first removed from the mineral sample. To this end, the radioactive constituents of the mineral were concentrated, before adding the tantalum to protect the protoactinium in carnotite, by sliming with dilute nitric or sulfuric acid, which leaves the bulk of the sand in an inactive residue. It was found that the sand was inactive only after sliming off about six times and only the coarsest sand remained. Small quantities of silica carried over in this operation gave no particular trouble in the precipitation of the tantalum and they were finally removed with hydrofluoric acid. In fairness to the bisulfate method of Hahn and Meitner, it may be said that great quantities of silica in all methods investigated gave serious trouble.

The best results were obtained when carnotite was dissolved in about twenty per cent. sulfuric acid instead of dilute nitric acid, using about ten cubic centimeters of the acid per gram of sample and sliming off as indicated above. The main advantage of using sulfuric instead of nitric acid lies in the fact that sulfur dioxide reduces vanadic salts very readily in the presence of sulfuric acid, but not in the presence of nitric acid. It was found that tantalum precipitates much more readily and in better form in the presence of the reduced vanadium salts. The solution was filtered and the tantalic oxide added to the dried residue and fused with potassium hydroxide in a nickel crucible. After the fusion was dissolved in cold water, there was practically no evidence of a precipitate and it was not filtered. The alkaline solution was then added to the acid solution and sulfur dioxide passed in until the vanadium was reduced to a lower state of valence, as indicated by the change in color. Ammonium hydroxide was added to incipient precipitation of uranium and perhaps some vanadium, and the solution boiled to precipitate the tantalum. Traces of barium sulfate and other insoluble sulfates appear immediately and later on the tantalum precipitates in a form which settles readily.

A difficulty here is apparent, that is, the barium–radium sulfates are brought down with the tantalum. Any number of bisulfate fusions would not remove the barium. The problem of separating the radium from the tantalum here offered one of the greatest difficulties of all in the work on carnotite. At first an attempt was made to remove most of the barium sulfate by letting it settle out before boiling the solution to precipitate the tantalum. After the solution had stood for forty-eight hours, it was decanted and filtered from the insoluble sulfates and the tantalum precipitated in the filtrate. This, on six different samples, showed that even in the cold about four-fifths of the tantalum was carried down with the barium sulfate.

Since the barium sulfate carries down most of the tantalum, even in the cold, there is no gain in trying to remove most of it by letting it settle out prior to boiling to precipitate the tantalum. On the contrary, it is best to boil the solution and precipitate the tantalum immediately after adding the ammonium hydroxide. The precipitate, consisting of tantalic acid, barium sulfate, some silica and so forth, may be allowed to settle and most of the supernatant liquor decanted before filtering, or it may be filtered through paraffined funnels as soon as it is cool, and treated with dilute hydrofluoric acid and ammonium hydroxide, as described under the bisulfate method.

In order to determine how many precipitations by the ammonium hydroxide would be necessary to remove the radium, the following experiment was carried out. Three ten-gram samples of carnotite were carried through the above procedures and filtered into paper cartons lined with paraffin. These filtrates were each diluted to about one hundred cubic centimeters and a little barium chloride solution was added to each. Since the sulfate is much more insoluble than the fluoride, a few drops of dilute sulfuric acid was added to each of them, and then each solution stirred with a platinum wire. The precipitate of barium sulfate and barium fluoride was allowed to settle for at least forty-eight hours, and then the solution was filtered through a good quality of filter paper and thoroughly washed. These papers were flattened out, dried and then placed in the chamber of an α-ray electroscope. In this particular instrument they had an average activity of 169.5 divisions per minute, and all ran very closely the same. The solutions were again treated with barium chloride and sulfuric acid, as before, and again allowed to stand for forty-eight hours. After filtering, washing and drying, the residues had the following activities in divisions per minute: No. 1, 0.13; No. 2, 3.35 and No. 3, 8.66. These divergencies are to be expected since no special care was used in the preparation of the films. They would normally, under the conditions, vary in concentration, area and thickness. After a third treatment, as outlined above, except that this time they were filtered through two thicknesses of filter paper, they had the following activities, in divisions per minute: No. 1, practically no activity on either filter paper; No. 2, 0.75 on the upper paper and 0.087 on the lower paper and No. 3, practically no activity on either filter paper. After a fourth treatment there was negligible activity in all three samples. The solutions were now made ammoniacal and the tantalum precipitated. This clearly indicates that if the tantalum is precipitated in the presence of the barium and radium carried through by the hydrofluoric acid treatment of the original residues, it is contaminated, and would certainly give untrustworthy results. In all of the experiments the results of which are recorded in this paper, the above operation was carried out from four to five times, depending on the mineral. By careful work, it is easy to recover upwards of ninety per cent. of the tantalum.

Thorianite.—The method of Russell and Widdowson, modified as indicated above, readily lends itself to thorianite. After grinding the mineral, it is treated with about forty per cent. nitric acid, using fifteen cubic centimeters of the acid per gram of sample. By gentle heating it is easily put into solution in less than a half hour. The solution is diluted, filtered and the residue dried and fused with potassium hydroxide in a nickel crucible. The tantalic oxide is added to the potassium hydroxide fusion. When quantitative results are desired, it is best to fuse the potassium hydroxide until vigorous action ceases and then drop the tantalic oxide into the crucible. It may be carefully brushed in, or put into a small piece of paper and dropped in. This procedure lessens the danger of losing any of the tantalum during the vigorous part of the reaction. The heating is continued until there is complete fusion, and since this tantalum is to bring out all of the protoactinium, it is best to keep it in a state of fusion at least fifteen minutes. The melt, after it has cooled, is dissolved in cold water. In the case of thorianite, the precipitate formed when the potassium hydroxide fusion was dissolved in water was very small, and since it was found to be very soluble in nitric acid, it was not removed. The potassium hydroxide solution is now added to the original nitric acid solution, then a few cubic centimeters of dilute sulfuric acid, and ammonium hydroxide to incipient precipitation of the uranium and thorium. The tantalum readily precipitates after boiling the solution for a few minutes. Since this particular mineral was relatively rich in radium, the tantalum precipitate was dissolved in hydrofluoric acid and precipitated with ammonium hydroxide, and this operation repeated four times in order to remove the last traces of radium. The final precipitate of tantalum was dried and fused with potassium bisulfate and the silica removed with hydrofluoric acid. The residue was finally weighed as tantalic oxide.

Soddite.—Soddite is a combination of uranic oxide, silica and water of hydration. It was treated in precisely the same way as thorianite. It required about three quarters of an hour to bring it into solution. In order to get the tantalum to precipitate, ammonium hydroxide must be added until considerable uranium is brought down and the precipitate is quite bulky. This precipitate is filtered out, ignited and then treated with nitric acid. The reason for igniting it is to change the tantalic acid to tantalic oxide, as freshly precipitated tantalic acid is quite soluble in mineral acids. The greater part of this ignited precipitate went into solution in the nitric acid. The residue remaining from the nitric acid treatment was filtered, washed and fused with potassium bisulfate, mainly to bring the tantalum into a condition in which it is readily soluble in dilute hydrofluoric acid. Upon boiling the bisulfate fusion in water, the tantalum readily separates out. This solution was filtered through a paraffined funnel, the precipitate washed and repeatedly treated with hydrofluoric acid and ammonium hydroxide as in the case of other minerals. The precipitate was finally thoroughly washed, dried and the silica removed in the regular way. To obtain a better texture, it was fused with potassium bisulfate, leached out and finally ignited to tantalic oxide.

Pitchblende.—The pitchblendes were treated in precisely the same way as the thorianite. The lead sulfate was more marked in the pitchblendes than in the other minerals, because of their much higher uranium content. In all cases, the repeated treatment of the precipitates with dilute hydrofluoric acid and ammonium hydroxide removes the lead. This treatment also puts the tantalum through the same chemical processes as were followed with the other minerals. As with the other minerals, the tantalum precipitate was finally fused with potassium bisulfate, not only to purify it, but to put it into better form. In all this work samples ranging from three grams, in the case of pitchblendes, to ten grams in the case of carnotite, were used.

With all the minerals studied, the method outlined above gave excellent quantitative results when one considers the great number of chemical manipulations involved and the recovery of the twenty milligrams of tantalic oxide which was added in each case. In most cases upwards of ninety per cent. of the tantalum was recovered, and in many cases the recoveries were considerably higher than this. While it is important to obtain good quantitative results, it is more important to see to it that the samples have been fused long enough to bring the tantalum in contact with all of the protoactinium. Fundamentally, a quantitative return on the tantalic oxide added to the sample is unnecessary, if the recovered oxide is pure. The activities of the films made from the tantalic oxide recovered depends on the amount of protoactinium present in the sample, hence the activity due to all of the protoactinium in the sample of mineral can be computed from films of known weight, provided the weight of the tantalum added to the original sample is known. The total activity, divided by the weight of the sample in grams, gives the activity due to the protoactinium in one gram of the mineral.

To prove that the activities of the protoactinium films furnish a true measure of the quantity of the protoactinium in minerals, the following sets of separations were carried out. The protoactinium was separated from three different minerals, using samples of different weight, but adding the same weight of tantalic oxide to each sample. Uraninite, thorianite and carnotite were used in these tests. For uraninite and thorianite, three three-gram and three six-gram samples were used. For carnotite, three five- and three ten-gram samples were taken. Twenty milligrams of tantalic oxide was added to each of the eighteen samples and then the samples were processed as described.

Films of the tantalic oxide recovered from each sample were made, weighed and their activities measured. From the weight of the film and its activity, the activity of twenty milligrams of film was computed. This value represents the α-ray activity of all the protoactinium in the sample of mineral taken.

Normally the tantalic oxide recovered from the larger samples should be twice that from the smaller samples and the activity per gram of mineral should be constant for each mineral, but different for the different minerals.

The averages of the total activities, in divisions per minute, and the ratio of the two activities, are given in the following tabulation.

Mineral	Av. small samples	Av. large samples	Ratio
Uraninite	7.46	15.32	2.05
Thorianite	4.31	9.40	2.18
Carnotite	8.73	17.66	2.02

The individual readings vary from 3.6 to 12.9% from the average readings given above. The eighteen samples were put through the same chemical processes as nearly as possible. Except in the case of the inactive sand from carnotite, the tantalum was precipitated in the presence of the whole sample in solution, that is, there was no chance for the division of the protoactinium between residue and solution in any stage of the analysis. The double quantity of protoactinium extracted when the mineral samples were doubled clearly established the reliability of the method followed for the quantitative separation of protoactinium from different types of uranium minerals.

The activities of the numerous protoactinium preparations obtained in this investigation were measured in an α-electroscope. The general idea for the use of the films was taken from Boltwood.[10] The material to be measured was painted on thin aluminum disks eight centimeters in diameter. These disks were turned in such a way as to have a rim about one millimeter high. The rim not only protects the film to some extent, but it keeps the very thin disk perfectly flat. The rims were so low that no correction was made for α-particles that may have encountered them. Before shaping the disks, one surface of the thin sheet aluminum was thoroughly rubbed with steel wool. This surface was then rubbed with

[10] Boltwood, *Am. J. Sci.*, [4] **25**, 176 (1908).

clean cotton until all free particles of aluminum were removed. This treatment produced a very slightly roughened surface upon which films can be painted more uniformly than on smooth aluminum. Material to be painted on these disks was ground very fine in an agate mortar and a suspension formed by adding a few drops of acetone. After trying different methods for painting films on these disks, it was found that small tufts of cotton, tightly rolled and held with small tweezers, were as good as anything tried. A small camel's hair brush works fairly well, except that in using the very small amount of material necessary in this work, practically all of it would be drawn up into the brush. Then too, a new brush would be required for each new preparation because of the possibility of contamination. The use of small pieces of cotton avoids both these difficulties.

In making measurements, one of these clean disks was placed in the chamber of the electroscope, in each case, before the natural drift was taken, to screen off any activity that might be in the chamber floor, as constant use of the instrument is liable to leave traces of active material on the bottom of the chamber. To reduce absorption of the radiations by the material to a negligible value, the films were made very thin, never containing over 0.2 mg. of material per square centimeter and in most cases less than this amount. Experiments showed that for thicker films there is a rapid falling off of activity with increase in weight.

The chamber of the electroscope used in all of these measurements was of such dimensions that the full range of the particles was utilized except for a negligible fraction. The activities were measured from time to time over a period of a year or more, and the activities, in divisions per minute, were computed on the basis of a gram of mineral in each case. A typical example: a 5.7-mg. film made from the tantalic oxide recovered from a ten-gram sample of carnotite gave a reading of 6.52 divisions per minute. Twenty milligrams of tantalic oxide had been previously added. The activity of all the protoactinium in the sample is $20/5.7 \times 6.52$ or 22.9 divisions per minute, and for one gram of the mineral the activity due to the protoactinium is 2.29 divisions per minute.

The initial activity due to the protoactinium in one gram of each of the minerals was obtained by plotting the activities, in divisions per minute, obtained as above, on the axis of ordinates, and the time, in days, on the axis of abscissas, and extending backward the growth curve to the axis of ordinates. The values obtained and their probable errors are given in Col. 4, Table I. The probable errors shown are based on at least six initial activities for each mineral.

To convert these initial activities due to the protoactinium in the different minerals, into atom for atom relations between protoactinium and uranium, it is necessary to know the α-ray activity of a gram of pure uranium, the percentage of uranium in the mineral and the α-ray activity due to the uranium in one gram of mineral.

In order to determine the α-ray activity of one gram of pure uranium, seven films of pure urano-uranic oxide, of the same dimensions as those above, were prepared and measured. The urano-uranic oxide used had been carefully freed from radioactivity by the method of McCoy.[11] The films varied in weight from 4.1 to 7.2 milligrams, and gave an average activity of 359.7 divisions per minute, per gram of oxide, or 423.9 divisions per minute, per gram of uranium element. The value 415.4 was obtained after deducting two per cent. due to the ionization of uranium X and uranium Y.[12] The average weight of the seven films was 4.9 milligrams, and since they had an area of 50.3 sq. cm., the average weight per square centimeter was approximately 1×10^{-4} grams. Johnstone and Boltwood[13] found that for films of approximately the same diameter as these, and weighing not more than ten milligrams, the absorption of the α-radiation was negligible. The probable error for the α-ray activities of the seven films was ±9.1 or about 2.2 per cent., when computed on the basis of one gram of uranium element.

The uranium content of the pitchblendes, soddite and carnotite were determined by the writer, using the emanation method. The value for the uranium content of thorianite was one made gravimetrically by Moore and Schlundt.[14]

Furthermore, the uranium content of the pitchblendes and soddite was very carefully determined, gravimetrically, by Mr. Fred Kavanagh, using the Randall[15] modification of the Boltwood[16] method for the determination of uranium in uranium minerals. The method used for the analysis of carnotite was that described in Bulletin 212, U. S. Bureau of Mines.[17] The value for carnotite was duplicated by an analysis made by Le Doux and Co.

The analytical results which follow give the percentage of uranium element in the different minerals.

Mineral	Emanation method	Gravimetric method
Carnotite, Colorado	20.43	18.65
Pitchblende, Bohemia	58.83	60.71
Pitchblende, Bohemia	62.22	62.98
Soddite, Belgian Congo	43.98	44.70
Thorianite, Ceylon	...	26.75

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[11] McCoy and Ashman, *Am. J. Sci.*, **26**, 521–530 (1909).

[12] Russell and Widdowson, *Phil. Mag.*, **46**, 920 (1923).

[13] Johnstone and Boltwood, *ibid.*, **40**, 55 (1920).

[14] Unpublished results.

[15] Randall, *J. Am. Electrochem. Soc.*, **21**, 463–497 (1912).

[16] Boltwood, *Phil. Mag.*, **9**, 603 (1905).

[17] Bulletin 212, U. S. Bureau of Mines, pp. 225–226.

The gravimetric values given above were used in all the calculations. The α-ray activity, Col. 3, Table I, due to the uranium in one gram of mineral was obtained in each case by multiplying the arbitrary constant 415.4 by the percentage of uranium in the mineral.

In order to reduce the measured protoactinium activities, Col. 4, Table I, to values corresponding to an equal number of uranium atoms, the protoactinium activities were multiplied by 61/72. This factor was determined as follows. According to Meyer and Schweidler[18] one α-particle from uranium I produces 1.16×10^5 pairs of ions in air over its entire range, and one α-particle from uranium II produces 1.27×10^5 pairs, the average being 1.22×10^5 pairs. One α-particle from protoactinium produces 1.44×10^5 pairs of ions in air over its entire range, hence the ionization due to the protoactinium is about fifteen per cent. greater atom for atom disintegrating than the average of that from uranium I and uranium II. To convert the protoactinium values to corresponding uranium values, they must be multiplied by the ratio $1.22 \times 10^5/1.44 \times 10^5$ or 61/72. These reduced values are given in Col. 5, Table I.

To illustrate the method of calculating the atom for atom relation, let us consider the sample of carnotite containing 18.65% of uranium element. The α-ray activity due to the uranium in one gram of the mineral is 415.4 × 0.1866 or 77.5 divisions per minute. The initial α-ray activity of the protoactinium in one gram of this mineral is 2.36 divisions per minute, and this times 61/72 equals 2.00 divisions per minute, which is the activity it would have if the α-particles from protoactinium had the same range as the average of those from uranium I and uranium II. Dividing 2.00 by 77.5 gives 0.0258, which is the ratio between the number of protoactinium atoms and atoms of uranium I and uranium II disintegrating in unit time. Multiplying 0.0258 by 2 gives 0.0516, or the ratio between the number of protoactinium atoms and atoms of uranium I or uranium II disintegrating. Multiplying 0.0516 by 100 gives 5.16, which is the number of atoms of protoactinium disintegrating per one hundred atoms of uranium I or uranium II. The values obtained for the different minerals are given in Col. 6, Table I.

TABLE I

VALUES FOR DIFFERENT MINERALS

Mineral	Uranium element, %	U activity per gram of mineral	Pa activity per gram of mineral	Pa activities reduced	Atoms of Pa per 100 atoms of U I and U II disintegrating
Carnotite, Colorado	18.65	77.5	2.36 ± 0.053	2.00	5.16
Pitchblende, Bohemia	60.71	252.2	4.16 ± .063	3.52	2.79
Pitchblende, Bohemia	62.98	261.6	2.26 ± .088	1.92	1.47
Soddite, Belgian Congo	44.70	185.7	4.03 ± .080	3.41	3.67
Thorianite, Ceylon	26.75	111.1	1.64 ± .031	1.39	2.50

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[18] Meyer and Schweidler, "Radioaktivität," **1927**, p. 629.

Discussion

It is seen that the ratio of protoactinium to uranium in the five minerals studied is by no means constant. The result is not entirely contradicted by the investigations of others, who have concluded that the ratio between protoactinium and uranium is constant in different minerals, for their experimental results show considerable variation in this ratio.

Largely on other evidence, many writers[19] of recent years have advocated the theory that the actinium series springs from an unknown isotope of uranium. The values they have variously assigned for the atomic weight of this isotope of uranium are 235, 237, 239 and 240.

The arguments in favor of an independent origin of the actinium series have centered around one or more of the following considerations: (1) the atomic weight of uranium being 238.18 has been taken as evidence of the existence of a higher isotope of uranium. However, this apparent excess weight of 0.18 has been explained on the basis of the "packing effect" by Plotnikow.[20] (2) There is no parallel to the formation of a branched series featuring a dual α-ray change. The other cases of branching, as in the "C" members of the uranium, thorium and actinium series, form one branch in an α-ray change and the other branch in a β-ray change. (3) The assumption of an independent origin of the actinium series seems to be more nearly in accord with the Geiger–Nuttall relation. (4) The discovery of certain rings in some pleochroic haloes can be explained on such an assumption.

Of all the suggested atomic weights for this independent source of the actinium series, the value 235 at present seems to be the most probable. Aston[21] found a faint line in the mass spectrum of some lead tetramethyl made from uranium lead obtained from Norwegian bröggerite. He states that it cannot be due to lead as an impurity, because in ordinary lead 208 is about twice as strong as 207; neither can it be due to the products of radium or thorium. As he states, it is difficult to resist the conclusion that it is the end-product of the only other disintegration family, that of actinium.

Rutherford[22] likewise speculates regarding this isotope of lead, atomic weight 207, and concludes that it is highly probable that the mass 207 is mainly due to actinium lead and that the actinium series has its origin

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[19] Piccard, *Sci. Phys. Nat.*, [4] **44**, 161–164 (1913); Soddy and Cranston, *Proc. Roy. Soc. London*, **94A**, 385–404 (1917–1918); Adams, THIS JOURNAL, **42**, 2205–2280 (1920); Joly, *Proc. Roy. Soc. London*, **102A**, 682–704 (1923); Russell, *Phil. Mag.*, [6] **46**, 642–656 (1923); Russell, *Nature*, **111**, 703–704 (1923); **114**, 717 (1924); **120**, 545 (1927); Iimori and Yoshumura, *Int. Phys. Chem. Res. Tokyo*, **5**, 12 (1926); Wilkins, *Phys. Rev.*, **29**, 352 (1927).

[20] Plotnikow, *Z. Physik*, **28**, 339–341 (1924).

[21] Aston, *Nature*, **123**, 313 (1929).

[22] Rutherford, *ibid.*, **123**, 313–314 (1929).

in an isotope of uranium which he calls "actino-uranium." He states that it is simplest to suppose that its mass is 235 and that it undergoes first an α- and then a β-ray transformation into protoactinium. The β-ray body is probably to be identified with uranium Y discovered by Antonoff.[23] On this view the successive transformations follow the order alpha, beta, alpha, beta, and differ in this respect from the main uranium series, which follows the order alpha, beta, beta, alpha. He states that it is possible for it to follow the uranium mode of disintegration, if it is assumed that the "actino-uranium" has an atomic weight of 239, atomic number 92 and disintegrates in an α-ray change followed by two β-rays. No evidence of such β-ray bodies has been found.

If it is true that 207 represents the mass of actinium lead, then it represents the first accurate determination of the atomic weight of a member of the actinium series and indicates that the atomic weight of protoactinium is 231. Thus it seems very probable that the origin of the actinium series is, as yet, an undiscovered isotope of uranium and the series is independent of the main uranium series. The results of this investigation lend support to this view.

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Summary

1. Since tantalum is the nearest homolog of protoactinium, extensive work was done on simplifying and standardizing a method which, with slight modifications, was used for the quantitative separation of tantalum from different uranium ores.

2. The uranium and protoactinium contents of five uranium ores from widely separated localities were determined and the atom for atom relation between uranium and protoactinium was computed in each case.

3. The results show that the protoactinium–uranium ratio in the different ores is far from constant, and consequently strengthens the view, now held by some, that the actinium series springs from a source other than uranium II.

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[23] Antonoff, *Phil. Mag.*, **22**, 419 (1911).