

T H E

AMERICAN JOURNAL OF SCIENCE

[F O U R T H S E R I E S .]

ART. XXVIII.—*On the Ultimate Disintegration Products of the Radio-active Elements*; by BERTRAM B. BOLTWOOD.

IN a paper by Rutherford and Soddy,* the authors have called attention to the probability that an intimate knowledge of the composition of radio-active minerals will lead to the recognition and identification of the ultimate, stable products formed by the disintegration of the relatively unstable radio-active elements.†

It is an extremely impressive fact that it was from the somewhat meager information available on the occurrence of helium in radio-active minerals, and from the consideration of the data derived from the experiments of one of them on the nature of the expelled alpha particle, that in 1902 the same authors were enabled to make that brilliant prediction of the production of helium‡ which was afterwards confirmed by the experiments of Ramsay and Soddy.

The natural minerals represent chemical systems which are in most instances of extreme antiquity, their original formation having frequently taken place during the earliest geological periods of our planet. With the assistance of the data supplied by geology and mineralogy, it is often possible to assign the origin of a given mineral to some definite geological period and to arrange a series of different individuals roughly in the order

* Phil. Mag. (6), v. 576 (1903).

† “In the naturally occurring minerals containing the radio-elements these changes must have been proceeding steadily over very long periods, and, unless they succeed in escaping, the ultimate products should have accumulated in sufficient quantity to be detected, and should therefore appear in nature as the invariable companions of the radio-elements.”—*Rutherford and Soddy, loc. cit.*

‡ Phil. Mag. (6), iv, 582.

of their production, obtaining in this manner an approximate knowledge of their relative ages. In dealing with the question of radio-active change, where the element of time is such an important factor in the solution of nearly every problem, the advantages to be derived from the careful study of the radio-active minerals can therefore scarcely be overestimated.

From a knowledge of the chemical properties and the crystallographic, optical and other physical properties of a given mineral specimen, together with an understanding of its occurrence and of the other mineral substances with which it is found associated, it is generally possible to definitely determine whether the mineral was formed simultaneously with the mass of material or geological formation in which it now occurs, or whether it is of more recent production, having originated through the action of percolating waters or of subterranean vapors or gases on some original constituent. In the former case, when all available data indicate that the formation of the mineral was coincident with that of the mass of rock in which it occurs, the mineral can be classed as primary; in the latter case, when it has apparently originated through the alteration of primary compounds, it can be considered as secondary. The term secondary can also be applied in a restricted sense to such minerals as occur in veins, where the general character of the vein indicates that it has originated through the formation of fissures in existing strata and that the contents of the vein is of an age inferior to that of the mass of rock by which it is bounded.

In applying these considerations to the greater number of minerals which have up to this time been observed to contain radio-active constituents, it may be considered as fortunate that these minerals occur under conditions which would seem to render the task of assigning the individual species to one or the other of the above classes a relatively simple one.

The most prominent radio-active mineral, uraninite, more commonly known as pitchblende, occurs both as a primary constituent of granitic rocks and also as a constituent of metalliferous veins cutting geological formations of a relatively recent geological period. When occurring in a granitic rock the uraninite is frequently quite perfectly crystalline in form and the rock itself is of the type called pegmatite; the most noted localities furnishing specimens of this primary uraninite being southern Norway, particularly in the neighborhood of Moss, North Carolina, Llano Co., Texas, and Connecticut. Prominent localities where uraninite occurs as a constituent of metalliferous veins are Johanngeorgenstadt, Marienberg and Schneeberg in Saxony, Joachimsthal and Příbram in Bohemia, Cornwall in England, and Colorado and South Dakota in the United States.

The term secondary uraninite will be used in referring to the material from these latter localities.*

Among the radio-active minerals other than uraninite which occur as primary constituents of pegmatite may be mentioned thorite, samarskite, fergusonite, aeschynite, euxenite, monazite and the recently described† thorianite. Associated with, and obviously resulting from the alteration of, the primary minerals through the action of percolating waters and other agencies, are secondary minerals, the more prominent of which are gummite, thorgummite, uranophane and autunite.

In considering the available data on the composition of radio-active minerals, with a view to discovering the ultimate disintegration products of the radio-elements, it is therefore necessary to give strict attention to the question of the primary or secondary origin of the individual specimens and the geological period at which they were formed. The nature of the associated minerals is also usually of considerable significance, since through them it is frequently possible to discover some clue to the conditions under which the mineral originated and some indication of the influences to which they have been subjected since they were first formed.

Lead.

In reviewing the various published analyses of minerals containing notable proportions of uranium, and particularly of those which are evidently of primary origin, one can not fail to be impressed by the frequent and almost invariable occurrence of lead as one of the other constituents. Out of a considerable number of analyses undertaken with the particular object of discovering whether or not lead was present, I have been unable to find a single specimen of a primary mineral containing over two per cent of uranium in which the presence of lead could not be demonstrated by the ordinary analytical methods. The same is moreover true of the secondary uranium minerals which have been examined, although in a single case, namely in a small specimen of uranophane from North Carolina, the proportion of lead was so low as to require the working up of a gram of material in order to conclusively demonstrate the presence of lead as a constituent.

Through a dawning appreciation of the significance of the persistent appearance of this element in uranium minerals, the writer was led to suggest in an earlier paper‡ that lead might prove to be one of the final, inactive disintegration products of uranium. All the data which have been obtained since that time point to the same conclusion.

* Hillebrand, this Journal, xl, 384 (1890).

† Dunstan and Blake, Proc. Roy. Soc. Lond. (A), lxxvi, 253 (1905).

‡ Phil. Mag. (6), ix, 613 (1905).

I have been particularly impressed by the information kindly supplied in a private communication by Mr. W. F. Hillebrand of the U. S. Geological Survey, a recognized authority on the analysis of uranium minerals, that so far as his experience goes he does not remember to have found uranium in any mineral without its being accompanied by lead, and he adds: "the association has often caused me thought."

Additional weight attaches to these experimental indications because of the theoretical considerations leading to a similar conclusion. It has been pointed out by Rutherford,* that if the alpha-ray particle consists of helium, since four alpha-ray products intervene between radium and the final, inactive substance radium-G, the indicated atomic weight of radium-G is sufficiently near to that of lead to be impressive. Thus one alpha particle is expelled by each of the atoms Ra, Ra-Em, Ra-A, Ra-C and Ra-F, making five particles in all. The loss of five alpha particles with an atomic weight of 4 from the atom of radium with an atomic weight of 225 would cause a reduction of this by $4 \times 5 = 20$ units, with the formation of a chemical element having an atomic weight of 205 or thereabouts. This is not far from the accepted atomic weight of lead, namely 206.9.

Thorium (Rare earths).

Another element which occurs quite commonly with uranium is thorium, and the common association of these two elements has been noted by Strutt and interpreted by him as indicating that thorium is possibly the parent of uranium.† Aside from the very doubtful hypothesis that the atomic weight of thorium is greater than that of uranium, his conclusions would seem open to serious objections. His statement that all thorium minerals contain readily detectable quantities of uranium, while some minerals containing notable quantities of uranium are comparatively free from thorium, is manifestly in accord with his experimental data, but it would appear that his thorium minerals containing uranium are all old minerals, while his uranium minerals containing no thorium are of relatively recent origin. If his theory is correct, the existence of very old minerals containing high percentages of uranium and no thorium should be possible, but that such minerals have been found is not indicated by any of the reliable analyses available. The experimental data offered by Strutt, as well as those to be derived from other sources, can all be much more consistently interpreted by the assumption that thorium is a disintegration product of uranium having a life considerably longer than that

* Silliman Lectures, Yale University, 1905. Not yet published.

† Proc. Roy. Soc. Lond. (A), lxxvi, 88 (1905).

of its parent and long as compared with the oldest of the known minerals. This hypothesis is supported by the circumstance noted by Strutt, that in general the minerals containing high proportions of thorium also contain a comparatively high proportion of helium, a point which will be referred to later in the course of this paper. Since the present knowledge of radio-active phenomena leads to the assumption that the average life of uranium is of the order of 2×10^9 years, while the average life of thorium is apparently in excess of that number, it seems scarcely reasonable to expect that minerals will be found which are sufficiently old for a state of equilibrium to have been reached between thorium and uranium. The production of a slowly changing disintegration product from a more rapidly changing parent is in no way contradictory to the disintegration theory, since a number of examples of this are at present recognized.* The common association of the other rare earths with thorium may indicate, as suggested by Strutt, that these are possible final products of the latter element.

Bismuth.

The occurrence of bismuth as a constituent of the more highly radio-active minerals is another significant indication of a possible end product. The proportion of bismuth which is present in the older radio-active minerals is, however, very small, so small indeed that its occurrence is but seldom detected in the ordinary course of analysis. It is only in treating considerable quantities of material for the extraction of polonium that the presence of bismuth becomes evident. This occurrence of bismuth in small quantities is suggestive of its formation from the disintegration, either of a parent having a relatively long life, or of one which is itself produced in only relatively small quantities. The former requirement would seem to be fairly well filled by thorium, in which case it is to be expected that in two minerals of equal age, the one containing the greater proportion of thorium would also contain the greater relative amount of bismuth. An opportunity has not yet been found for the experimental investigation of this question. The fact that the atomic weight of bismuth differs from the atomic weight of thorium by exactly 24 units, an even multiple of 4, is possibly significant.

Barium.

Another element which persistently appears as a minor constituent of uranium minerals is barium. Its production, if it is

* One example is the production of the active deposit from the thorium emanation, the parent with a half-value period of less than one minute, the product with a half-value period of eleven hours.

actually a disintegration product, is certainly slow, for only very small relative amounts of it are found in some comparatively old minerals. In primary minerals the amount of lead present is always greatly in excess of the barium, which occurs only in traces made evident in the separation of the radium from considerable quantities of material. As in the case of bismuth, the barium might be produced either from a slowly disintegrating parent or from a radio-active body existing only in comparatively small amounts in the radio-active system. Certain data, to be published later by the writer, have been obtained which seem to indicate that the amount of actinium in a radio-active mineral is dependent on the amount of uranium present, thus suggesting that uranium is the parent of actinium as well as of radium, but other results lead to the conclusion* that actinium is not a direct result in the same sense as is radium. The quantity of actinium produced in a radio-active mineral is apparently small as compared to the radium, and it may therefore be possible that the barium present is a final product of the actinium.

Hydrogen.

A point which has caused much speculation on the part of mineralogists is the apparent hydration of the greater number, if not all, of those minerals which are now known to contain radio-active constituents. That this state of affairs is in some way connected with the disintegration processes taking place in these compounds would not appear impossible, since the production of such an elementary substance as hydrogen as one of the products of the radio-active decay of the atoms of elements of high atomic weight is in fact suggested by much of the data on the nature of the expelled alpha particles.† It would seem possible that the difference in ionizing power, of the power of penetration, etc., shown by the alpha particles from certain of the radio-active types of material may perhaps be due to a difference in the mass of the projected particle, and that the occurrence of notable quantities of water in the primary radio-active minerals, which is otherwise most difficult to explain, may be considered as indicating that hydrogen is in fact one of the disintegration products, originating as an alpha-ray particle from one or more of the numerous radio-active substances which have already been identified. The origination of hydrogen in a mineral containing oxidized constituents would in all probability lead to the reduction of the more readily reducible of these with the consequent production of water.

* Rutherford and Boltwood, this Journal, xx, 56 (1905).

† Rutherford, "Radio-activity," p. 328 and elsewhere.

In the greater number of instances where water is found present in these minerals, it is quite impossible to explain how it could have penetrated into them from without, since their close-grained and impervious nature is impressively indicated by the very notable quantity of helium which they have retained. Moreover non-radio-active minerals which occur associated with the radio-active species, and which have been subjected to the same external influences, are often quite anhydrous, e. g., apatite, magnetite, etc. The mineral thorite has been called to the attention of the writer by Professor S. L. Penfield. This mineral frequently occurs in very perfect crystals, which however exhibit only the optical properties of an isotropic and amorphous compound. This species has been long regarded as having undergone alteration, but that the causes of the alteration existed within and not without the crystals is, I believe, a new and somewhat novel explanation.

It is a significant fact that results obtained* in the examination of certain radio-active minerals indicate that hydrogen occurs as one of the gaseous constituents of many of these compounds. A further interesting point bearing on this question is mentioned by Hillebrand,† who observed that when uraninite was mixed with sodium carbonate and fused in an atmosphere of carbon dioxide, the lead present was apparently entirely reduced and collected in globules. Mixtures of corresponding proportions of lead oxide (litharge) and U_3O_8 or UO_2 , when treated in an identical manner, showed no reduction of the litharge to metallic lead. This distinctive difference in behavior is strongly indicative of the presence of hydrogen as a constituent of uraninite.

Argon.

Results obtained by Ramsay and Travers‡ may further indicate that another of the disintegration products of radio-active substances is the inert gas argon. It is stated by these authors that most minerals which evolve helium also evolve argon in small quantity. It may not be impossible that some of the rayless changes which have been observed by Rutherford to take place in radio-active bodies, may be accompanied by the expulsion of alpha particles consisting of argon, which owing to their relatively high mass are projected at too low velocities to cause ionization of the surrounding gases and to permit

* Ramsay, Collie and Travers, Jour. Chem. Soc., Lond., lxxvii, 684 (1895), state that hydrogen in varying quantities was evolved by ytrotantalite, samarskite, hielmite, fergusonite, tantalite, monazite, xenotime, columbite, perovskite, euxenite, orthite, gadolinite and cerite. Also Ramsay, Proc. Roy. Soc. Lond., lix, 325 (1896).

† Bulletin of the U. S. Geological Survey, No. 78, p. 59 (1891).

‡ Proc. Roy. Soc. Lond., lii, 316 (1898).

their detection by the ordinary electrical methods. It has been pointed out by Rutherford* that the kinetic energy of certain alpha particles approaches quite closely to the critical value below which no ionization would be produced. It is moreover quite interesting that the assumption of a difference of atomic mass of 40 units between certain successive radio-active transformation products would greatly facilitate their assignment to vacant positions in the periodic system of the elements.

Composition of Uraninite.

The suggestions offered in the foregoing pages as to the possible nature of some of the disintegration products resulting from the process of radio-active change can be more clearly understood, and the basis of fact from which they have been derived can be more correctly appreciated, by a consideration of some of the results which have been obtained in the analysis of radio-active minerals.

The most accurate and reliable of the available data on the composition of uraninite have been published by Hillebrand.†

TABLE I.

Locality Number.	Glastonbury, Conn.					Branchville, Conn.			Colo.	N. Carolina.	
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
UO ₃	22·08	23·35	22·22	26·48	23·03	13·27	21·54	14·00	25·26	50·83	44·11
UO ₂	59·13	58·01	59·31	57·43	59·93	72·25	64·72	70·99	58·51	39·31	46·56
Total Uranium	70%	70	70	72	72	74	75	74	72	77	77
PbO	3·14	3·24	3·07	3·26	3·08	4·35	4·34	4·35	0·70	4·20	4·53
ThO ₂	----	----	----	9·79	----	7·20 ²	6·93	6·52 ²	0·0	2·78	
Total rare earths	9·57	10·24	10·31	10·37	11·10	7·20	7·26	6·52	7·81	3·74	3·04
N ₂ ¹	----	----	----	----	2·41	----	----	2·63	0·15	0·37	
H ₂ O	0·97	----	----	0·61	0·43	0·68	0·67	0·68	1·96	1·21	
Sp. G.	9·12	9·05	----	9·58	9·62	9·73	9·56	9·35	8·07	9·08	9·49

Various important details such as the general character and appearance of the different samples and the indication of alteration from external causes in a number of specimens will be found in Hillebrand's papers.

Blank spaces in the table signify that the indicated constituent was not determined.

¹ Hillebrand assumed that the inert gas present was nitrogen and the percentages of this element shown in the table are calculated on the basis of that assumption. By dividing these numbers by 7 a maximum value for the helium separated is obtained.

² ThO₂ + ZrO₂ ?

The results of his analyses are given in a condensed form in Table I.

* Phil. Mag., July (1905).

† Bulletin of the U. S. Geological Survey, No. 78, p. 43, 1891; this Journal, xl, 384 (1890); *ibid.*, xlii, 390 (1891).

Neglecting for the present the results under IX and XXII, which are types of secondary uraninites, it will be noticed in an examination of the numbers given in Table I that—

1. In specimens from the same general locality, viz.: from Connecticut, from Norway and from North Carolina, a rough proportionality is shown between the content of uranium and the content of lead, rare earths, helium (nitrogen) and water. A still more striking relation appears to exist between the proportion of uranium in the form of the lower oxide, UO_2 , and the amount of helium (nitrogen). This was remarked by Hillebrand, who makes the following statement* in connection with the results obtained from the analysis of the first eighteen samples:

“Throughout the whole list of analyses in which nitrogen has been estimated the most striking feature is the apparent relation between it and the UO_2 . This is especially marked in the table of Norwegian uraninites recalculated†, from which the rule might almost be formulated that, given either nitrogen or UO_2 the other can be found by simple calculation. The same ratio is not found in the Connecticut varieties, but if the

TABLE I.

Norway.							Texas.	S. Carolina.	Canada.	Saxony.
XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI.	XXII.
30.63	25.36	22.04	32.00	35.54	42.71	26.81	44.17	----	41.06	59.30
46.13	50.74	43.03	43.88	43.38	24.18	44.18	20.89	----	34.67	22.33
66	66	57	65	68	56	61	55	71	65	68
9.04	10.06	8.58	9.46	9.44	10.54	10.95	10.08	3.58	11.27	6.39
6.00	8.48	----	8.98	6.63	----	4.15	6.39	1.65	6.41	0.0
7.62	9.03	8.43	10.48	8.09	13.42	13.87	19.19	10.25	10.49	0.0
1.17	1.28	1.08	1.03	1.08	----	1.24	0.54	----	0.86	0.02
0.74	0.73	0.74	0.77	0.79	1.23	----	1.48	----	1.47	3.17
8.89	9.14	8.32	8.96	8.93	7.50	----	8.29	----	----	6.89

Of the samples from Norway XII was from Anneröd, XIII and XIV from Elvestad, XV from Skaartorp, XVI from Huggenäs-kilen, and XVII and XVIII from Arendal. Sample XIX was from Llano Co., Texas, XX from Marietta, South Carolina, XXI from Villeneuve, Canada, and XXII from Johannegeorgenstadt, Saxony.

determination of nitrogen in the Branchville mineral is to be depended on, the rule still holds that the higher the UO_2 the higher likewise is the nitrogen. The Colorado and North Carolina minerals are exceptions, but it should be borne in mind that the former is amorphous like the Bohemian and possesses the further similarity of containing no thoria, although zirconia may take its place, and the North Carolina material is

* This Journal, xi, 391 (1890).

† Excluding the insoluble matter.

so much altered that its original condition is unknown." This generalization can apparently be extended to include lead also.

2. When the analyses of samples from the same actual locality are compared it will be evident that, in general,

a) The content of rare earths increases with the amount of lead present. This is most strikingly shown in the groups I-V, VI-VIII, XIII-XIV and XVII-XVIII. The simultaneous variation of thorium is also indicated somewhat imperfectly in those instances where this constituent was separately determined.

b) That in those specimens having the highest specific gravity (V and VIII) the proportion of helium compared with the lead present is greatest. It is in general to be expected that the denser and therefore less porous material would retain a greater proportion of the helium formed within it. The low proportion of gas compared with lead in X and XIX might well be due to the high emanating power of the former* and the greater porosity of the latter indicated by its low density. It is moreover interesting to note that those specimens (X, XIX, XXI) containing disproportionately large amounts of water contain a relatively low amount of helium compared with the lead present. It is possible that these minerals were sufficiently porous to permit the entrance of water from without while at the same time a part of the helium formed has escaped from within them.

It is evident that, in Table I, a lack of agreement exists between the proportion of lead and rare earths and the proportion of helium in the Connecticut material and the proportions of the corresponding constituents in the Norwegian samples. In the latter the amounts of lead and rare earths as compared with the gas present are much greater than in the former. This can be explained by assuming that the Norwegian minerals are considerably older than the American varieties, and that the Norwegian specimens examined by Hillebrand have in some manner lost a large part of their helium. The geological data available on the relative ages of the American and Norwegian occurrences, while not entirely in accord with the assumption of such a great difference in age, would not appear to be sufficiently definite to preclude such a possibility.

In considering the bearing of the results of the analyses of the two secondary uraninites, IX and XXII, on the general theories proposed in this paper, it is evident that the presence

* *Phil. Mag.* (6), ix, 609.

of the low proportion of lead and helium, and the practical absence of thorium in IX, is quite in accord with the geological indications that this material is of an age greatly inferior to that of the primary uraninites. In XXII the very notable amount of lead shown by the analysis would seem to offer no serious obstacle to the theory, since this material occurs intimately associated with the sulphide of lead and other similar minerals, and the massive and amorphous form in which it is found would indicate that the conditions under which it was originally deposited were not favorable to the separation of a pure uranium compound. The statement of Hillebrand* that nitrogen (helium) and the rare earths were practically absent in specimens of secondary uraninite from Pibram, Joachimsthal and Johanngeorgenstadt, which he examined, is also of interest in this connection. The experience of Debiernet† in separating actinium from a secondary uraninite of this character, is, however, indicative of the existence of small amounts of thorium in these minerals.

Other Radio-active Minerals.

In the table which follows (Table II) will be found some data compiled from various sources on the composition of a number of primary and secondary radio-active minerals.

As bearing on the topic under discussion it is interesting to note the following :—

1. The greatest proportion of helium with respect to the uranium and lead present has been observed in those primary minerals which have the lowest emanating power and the highest specific gravity, i. e., in the most compact and least porous minerals. Examples are furnished by thorianite, fergusonite, samarskite and monazite. (Of the varieties of thorite, much greater proportions of helium have been observed in the variety known as orangite, which has also the greatest density.)

2. Greater proportions of lead and helium with respect to uranium are found in those primary minerals which occur in the oldest geological formations. This point is well illustrated by thorianite, which is found in Ceylon in a geological formation which is probably of the Archean period.

3. The primary minerals containing the greatest proportion of thorium are in general the most hydrated.

In considering the secondary radio-active minerals certain probable conditions must be recognized. Where these minerals are formed by the alteration of primary minerals *in place*, namely, where the primary mineral is acted on by underground

* Bulletin U. S. Survey, No. 78, p. 72.

† Compt. rend., cxxx, 906 (1900).

TABLE II.

PRIMARY MINERALS.							
Species.	Locality.	ThO ₂	UO ₂	PbO	H ₂ O	He	Reference.
Thorite, Hitterö, Norway	----	48.66	9.00 ¹	1.26	10.88	X ^a	Dana, p. 488
Mackintoshite, Llano Co., Tex.	----	45.30	22.40	3.74	4.31	X ^b	A ₁
Yttrialite, Llano Co., Tex.	----	10.85	1.64	0.80	0.32	X ^c	A ₂
Thorianite, Ceylon	----	78.86	----- ²	2.59	X ^d	0.39%	A ₃
Samarskite	----- ³	10-13%	-----	3-1%	X ^e		
" (?) Colorado	----	3.64	4.02	0.72	1.58	?	Dana, p. 740
Annerödite, Anneröd, Nor.	----	2.37	16.28	2.40	8.19	?	Dana, p. 741
Euxenite	----- ³	5-12%	0.92	4.71	?		Dana, p. 744
Hielmite, Falun, Sweden	----	?	2.34 ⁴	0.21	2.23	X ^e	Dana, p. 742
Polycrase, Slättakra, Nor.	----	3.51	18.45	0.92	4.71	X ^e	Dana, p. 745
Fergusonite, Llano Co., Tex.	----	0.83	7.05 ⁵	1.43	2.02	?	Dana, p. 730
"	--	?	3.81 ⁴	0.16	?	0.03	A ₄
Xenotime, Narestö, Sweden	----	2.43	3.48 ⁴	0.68	1.77	X ^e	Dana, p. 749
Monazite, North Carolina	----	5.00	0.40 ⁶	tr.	0.20	X ^e	
SECONDARY MINERALS.							
UO ₃							
Gummite, North Carolina	----- ⁷	75.20	5.57	10.54	?		Dana, p. 892
Thorogummite, Llano Co., Tex.	----	41.44	22.43	2.16	7.88	?	A ₅
Carnotite, Colorado	-----	0.0	52.25	0.25	3.06	0 ⁸	A ₅
Uranophane, North Carolina	----- ⁹	66.67	0.60	12.02	?		Dana, p. 699

¹ U₂O₃.² UO₂ 6.03 + UO₃ 9.07.³ Hofmann and Strauss (Berichte, xxxiii, 3126) state that they found both thorium and lead in samarskite and in euxenite.⁴ UO₃. ⁵ UO₃ and UO₂.⁶ The composition of monazite given above is derived from experiments of the writer.⁷ Specimens of gummite from North Carolina analyzed by the writer have been found to contain from 2 to 3 per cent. of thoria.⁸ It is stated by Adams (this Journal, xix, 321 (1905) that helium is absent from this mineral, which is to be expected since it is highly porous and of recent formation.⁹ Samples of this material have been examined by the writer in which no thorium could be detected.X^a Helium has been found in the variety of thorite known as orangite.X^b Hillebrand's experiments suggest the presence of helium in this mineral.X^c Including this species among the primary minerals is possibly open to objection. Hillebrand's experiments would seem to indicate that it contains from 1^c to 2^c of helium per gram.X^d The analyses of Dunstan and Blake (see Ref.) do not indicate the presence of water, but several tests made by the writer, on samples kindly supplied by Mr. Geo. F. Kunz, suggest the presence of water in quite notable quantities.X^e The occurrence of helium in samarskite, hielmite, polycrase, xenotime, monazite, orangite, and other radio-active minerals is described in papers by Ramsay, Collie and Travers (Jour. Chem. Soc. Lond., lxvii, 684) and Ramsay and Travers (Proc. Roy. Soc. Lond., lx, 442).A₁ W. F. Hillebrand, this Journal, xlvi, 101 (1893).A₂ Hillebrand, this Journal, xiii, 195 (1902).A₃ Dunstan and Blake, Proc. Roy. Soc. Lond. (A), lxxvi, 253 (1905).A₄ Ramsay and Travers, Proc. Roy. Soc. Lond., lii, 316 (1898).A₅ Hillebrand and Mackintosh, this Journal, xxxviii, 480 (1889).A₆ Hillebrand and Ransome, this Journal, x, 120 (1900).

waters, etc., with the removal of certain constituents and the substitution of others originally dissolved in the waters, the resulting hydrated residue will in some cases consist of a mixture of several different chemical compounds and its general composition will not correspond to any definite formula, but will depend on chance and the accidental local conditions. An excellent example of a secondary product of this character is afforded by the mineral known as gummite, which occurs as an alteration product of the North Carolina uraninites. Samples of this mineral from the Flat Rock mine have been examined by the writer, in which great variations in the proportions of lead, thorium and uranium present were observed in samples removed from different parts of the same comparatively small specimen. The mineral known as uranophane from the same locality shows corresponding variations in composition. Both these substances are amorphous in structure but very frequently occur with a crystalline form as pseudomorphs after the original uraninite. It is obvious that these facts must be considered in attempting to arrive at any conclusions from a chemical examination of these materials.

In other cases the percolating waters undoubtedly dissolve the more readily soluble components of the primary minerals and deposit them again as definite, crystalline compounds of a relatively high degree of purity. Examples of this sort are afforded by such minerals as torbernite $[\text{Cu}(\text{UO}_2)_2\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}]$, autunite $[\text{Ca}(\text{UO}_2)_2\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}]$, uranocircite $[\text{Ba}(\text{UO}_2)_2\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}]$, zimmerite $[\text{Cu}(\text{UO}_2)_2\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}]$, uranosphaerite $[(\text{BiO})_2\text{U}_2\text{O}_7 \cdot 3\text{H}_2\text{O}]$, and a considerable number of others. The examination of minerals of this character will probably afford data of considerable value on the nature of the ultimate disintegration products of uranium.

The mineral mackintoshite is quite possibly of secondary origin, but owing to some doubt in the matter it has been placed among the primary minerals. It may represent a variety of thorite, containing originally a considerable proportion of uranium, which has undergone alteration owing to the radio-active processes which have taken place within it. The evidence is strongly in favor of the view that the thorogummite has been formed from the alteration of the mackintoshite through external causes.

Any definite conclusions at present as to the formation of carnotite are quite impossible. Its composition and occurrence are both so unique that little or no analogy with other known uranium compounds can be detected. It seems highly probable, however, that its age is not relatively very great and its general composition, *e. g.* the low amount of lead present and the practical absence of thorium and helium, is quite in accord with such a conclusion.

An interesting radio-active mineral has been described by Danne.* This substance is stated to be a phosphate of lead, or pyromorphite, containing quantities of radium equivalent to about 6 per cent of uranium. It is asserted, however, that no uranium is present in the mineral, although considerable deposits of uranium minerals are known to exist at no very great distance in the same region where it occurs. According to Danne, the pyromorphite is found in fissures through which underground waters containing radium salts are constantly percolating, and he suggests that the radium contained in the mineral is derived from the water. It might also be conjectured that the lead of the mineral has resulted from the disintegration of radium, the radium itself having been formed from the disintegration of uranium in the neighboring deposits.

Occurrence of Minerals.

It would seem possible that some general data on the disintegration products of radio-active substances might be derived from the study of the conditions under which the radio-active minerals occur in nature. The following suggestions may perhaps be of interest in this connection. The primary minerals found in the pegmatitic dikes include uraninite, thorite, fergusonite, aeschenite, euxenite, columbite and monazite, all of which, with the exception of columbite,† probably contain thorium in greater or smaller proportions. The theory generally accepted by geologists is that the pegmatites were formed under conditions of so-called hydro-igneous fusion, involving high temperatures and the presence of considerable water vapor which was prevented from escaping by the high pressure due to incumbent masses of rock of great thickness. Assuming the prior existence of considerable deposits of uranium compounds at great depths, it would appear probable that in an upheaval of deep-lying material, with the intrusion of the plastic magma into the upper layers from below, the conditions would be favorable to the separation of the various constituents of the already partially disintegrated uranium with the production of new minerals representing new combinations of the various elements present. Thus some of the uranium might separate out as the oxide (uraninite), either quite free from other elements or with admixtures of other isomorphous oxides (thorium oxides and other rare earth oxides), while the thorium might be greatly concentrated in the form of such minerals as thorite and thorianite, containing mixtures of variable propor-

* Compt. rend., cxi, 241 (1905).

† The very common association of radio-active elements with niobium, tantalum, etc., in minerals is possibly significant of some ultimate relation between them.

tions of uranium and the rare earths. Others of the rare earths present might be themselves concentrated to form such minerals as allanite and gadolinite, compounds containing but relatively small proportions of the radio-elements.

When uraninite is found in metalliferous veins the general indications point to its transportation hither from greater depths by thermal waters and its deposition at a temperature considerably lower than that existing in the plastic pegmatite. The association of the secondary uraninites with the sulphides of iron, copper, lead, bismuth and other metals is indicative of conditions of deposit unfavorable to the simultaneous production of rare earth minerals, which have never been observed to occur under similar conditions in any locality.

The mode of occurrence of radio-active minerals would therefore appear to offer certain valuable data on the processes taking place in the radio-elements and the products formed by their disintegration.

Origin of Elements.

If it can be ultimately demonstrated that lead, bismuth, barium, hydrogen and argon, or any one of them, actually result from the disintegration of uranium, an interesting question which naturally arises will be: Have the quantities of these chemical elements already existing been produced wholly in the same manner? Any discussion of this problem at the present time would certainly be premature, but the time may not be very far remote when this question will deserve serious consideration.

Summary.

Various data have been presented which are interpreted as indicating that the ultimate disintegration products of the radio-elements may include lead, bismuth, barium, the rare earths, hydrogen and argon.

The writer is fully conscious of the meagerness of the data upon which the hypothesis of the production of these substances is founded, but the suggestions are made in the hope that the attention of other investigators may be directed to the possibilities offered by a careful study of the composition and occurrence of the radio-active minerals, and that their interest may be sufficiently awakened to induce them to independently undertake the experimental investigation of the theories which have been suggested.