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*Conclusions.*

1. The ionisation produced per centimetre by  $\beta$ -particles in free air varies inversely as the square of the velocity between the limits examined.

2. The ionisation in a thick copper vessel is not connected with the velocity by any simple power law, but is approximately given by  $I = k(c-v)$ , where  $k$  and  $c$  are constants and  $v$  the velocity of the  $\beta$ -particles.

In conclusion, I wish to express my best thanks to Prof. Rutherford for proposing this research, and for his suggestions from time to time during its progress.

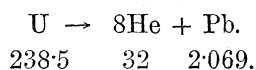
*The Association of Lead with Uranium in Rock-Minerals, and its Application to the Measurement of Geological Time.*

By ARTHUR HOLMES, A.R.C.S., B.Sc., Imperial College of Science and Technology.

(Communicated by Prof. the Hon. R. J. Strutt, F.R.S. Received March 20,—Read April 6, 1911.)

1. *Introduction.*—The study of radioactive minerals is of great importance from two points of view. Such minerals may be regarded as storehouses for the various series of genetically connected radioactive elements. In them the parent element slowly disintegrates, while the ultimate products of the transformation gradually accumulate. The analysis of these minerals ought, then, in the first place, to disclose the nature of the ultimate product of each series; secondly, a knowledge of the rate of formation of this product, and of the total quantity accumulated, gives the requisite data for a calculation of the age of the mineral.

It has been shown that the disintegration of uranium results in the formation of eight atoms of helium.\* In 1907 Boltwood brought forward strong evidence suggesting that lead is the ultimate product of this disintegration.† In this paper it is hoped to produce additional evidence that such is the case, according to the following equation:—



\* See Strutt, 'Roy. Soc. Proc.,' A, 1908, vol. 81, p. 276.

† Boltwood, 'Am. Journ. Sci.,' 1907, p. 77.

On the assumption that helium is produced to this extent, Rutherford has given data\* from which it may be calculated that 1 gramme of uranium produces  $10.7 \times 10^{-8}$  c.c. of helium per annum. Strutt has verified this theoretical estimate by a direct appeal to experiment.† Actually measuring the annual production of helium, he obtained a corresponding result of  $9.9 \times 10^{-8}$  c.c. Accepting the theoretical figure, which is equivalent to  $1.88 \times 10^{-11}$  gm., it is easily calculated that the amount of lead which would remain is  $1.22 \times 10^{-10}$  gm. per gramme of uranium per annum. If this rate of production were constant, a gramme-molecule of lead would take the place of a gramme-molecule of uranium in 8,200 million years. However, the rate is not constant, but is proportional to the amount of uranium remaining unchanged. If the latter is large compared with the total amount of lead produced, the rate may be taken as nearly constant, and the age of the mineral in which this disintegration has occurred is given by

$$\text{Pb/U} \cdot 8200 \times 10^6 \text{ years,}$$

where Pb and U represent the respective percentages of these elements at the present day. In many cases, however, this constancy cannot be assumed, and it is necessary to substitute for the present-day percentage of uranium its time-average for the period considered. Thus, in the minerals described in this paper, the difference between the uranium now present and that originally present amounts to about 5 per cent., and, in calculating the age, corresponding values are obtained. In this case a sufficiently accurate approximation to the time-average is given by the mean.

For minerals of the same age, the ratio Pb/U should be constant, if all the lead has originated as suggested. Further, for minerals of different ages, the value of Pb/U should be greater or less in direct proportion to those ages.

Collecting all the known analyses of primary uranium-bearing minerals which included a determination of lead, Boltwood‡ showed that the above conditions were generally found to hold. Unfortunately, he omitted to give the geological ages of the several occurrences. In a summary of his analyses, to be given in a later section, these will be indicated as accurately as at present is possible.

2. *Selection of Minerals.*—In order that the suggested relations between lead and uranium should be detectable, and that lead should be confidently used as a reliable age-index, certain assumptions require to be made. The selection of minerals must be such that for them these assumptions are justifiable. They will be considered as follows:—

\* Cited by Strutt, 'Roy. Soc. Proc.,' 1908, p. 276.

† Strutt, 'Roy. Soc. Proc.,' A, 1910, vol. 84, p. 388.

‡ 'Am. Journ. Sci.,' 1907, p. 77.

(a) That no appreciable amount of lead was present when the mineral was formed.

(b) That no lead has originated by any other radioactive process than that suggested.

(c) That no lead nor uranium has subsequently been added or removed by external agencies.

(a) Previously to the consolidation of a rock magma, the uranium in the latter must, of course, have been generating helium and lead for an unknown period. It is probable that much of the lead then present would, at the time of crystallization, be carried away in hot sulphide solutions to form the hydrogenetic and metasomatic deposits of lead which provide our supplies of that metal. Doubtless, however, a certain amount of lead would be retained in the molecular network of crystals, and consequently analyses of a rock as a whole should give values of Pb/U higher than that corresponding to the period since consolidation. This difficulty may be avoided by considering particular minerals. Thorite, zircon, in some cases apatite and sphene, and other rarer minerals segregate within themselves on crystallization a much larger percentage of uranium than remains to the rest of the magma. Within these minerals lead accumulates to such an extent that the amount originally present becomes negligible.

(b) It may be objected that lead may perhaps originate as a product of some element other than uranium. Boltwood shows that it is highly improbable that thorium should give rise to lead, and the results submitted in this paper add further proof to that independence. Wherever lead occurs in primary minerals it is associated with uranium, and there is little doubt that it can be completely accounted for in this way.

(c) It may seem unlikely that for periods of hundreds of millions of years a mineral should remain unchanged by external chemical agencies. In the earth's surface materials, making up the belt of weathering, solution is the dominant process. Lower down, in the belt of cementation, re-deposition is more characteristic.\* Can we be sure that these processes have not dissolved out lead or uranium at one time, depositing the same elements at another time? In some cases we cannot, but, fortunately for our purpose, many of the uranium-bearing minerals, like zircon, are dense and stable, and capable of withstanding great changes in their environment without undergoing alteration. But an appeal to analysis will rarely fail to dispel this difficulty. If such changes have occurred, it is inconceivable that they would always have affected lead and uranium in the same proportion,

\* See Van Hise, "Treatise on Metamorphism," 'Mon. United States Geol. Survey,' 1904, vol. 47.

and hence the results obtained from different minerals should show marked discrepancies. On the other hand, if the analyses give consistent results one can only assume that any alteration has been inappreciable. A microscopical examination of the minerals in question affords a useful guide to the extent of alteration. Unless one can be sure in this way that the mineral is fresh, it is clear that reliable results can only be expected when a series of minerals are examined.

Still another possible objection may be treated here. Under the high temperatures and pressures which rocks have undergone during their geological history, is it safe to assume that radioactive changes proceed at the same rate? All that can be said is that experimental evidence consistently agrees in suggesting that these processes are quite independent of the temperatures and pressures which igneous rocks can have sustained without becoming metamorphosed. Arrhenius has supposed that radioactive processes may be reversed under the conditions prevailing at great depths. This idea has nothing but analogy to support it. There is abundant evidence that molecular changes are reversed at greater depths, *e.g.*, in the upper zones of the earth's crust silicates are replaced by carbonates, while in the lower zones carbonates are decomposed and silicates are formed. But that interatomic changes should reverse, or even proceed more slowly or quickly, there is no evidence.

From these considerations, it is obvious that the only minerals to be chosen are fresh, stable, primary rock-minerals. Secondary and metamorphic minerals could not be relied upon to satisfy the required conditions. There occurs in the Christiania district of Norway,\* a geologically depressed area of nearly 4,000 square miles, which is separated on every side by faults from the surrounding Pre-Cambrian gneiss. In this area there is a nearly complete sequence of early palæozoic rocks. Above these strata there are a few beds of red sandstone of Lower Devonian age. Over these beds and intercalated with them are lava flows; and, finally, penetrating the whole mass, representing a later phase of this period of igneous activity, are great intrusions of plutonic rocks. Amongst the earliest of the intrusions is a series of thorite-bearing nepheline-syenites. Brögger believes them to be of Middle or Lower Devonian age, most probably the latter. The minerals occurring in them are, in many instances, notably radioactive, and thus they afford an admirable series in which to investigate the consanguinity of lead and uranium. Several of these minerals were obtained from Brevig, and estimations of these elements in each case were made.

\* See Brögger, 'Zeit. für Kryst.', 1890, vol. 16.

3. *Methods of Analysis.*—(a) *Uranium.*—This constituent was estimated by Strutt's method,\* in which radium emanation is directly measured, and the constancy of its ratio to uranium used to give the amount of the latter.

From 0.3 gm. to 2.0 gm. of the finely powdered mineral was used for each estimation, according to the relative richness of the mineral in uranium. From preliminary electroscopic tests this could be roughly measured. The powdered mineral was fused with borax in a platinum crucible, and the resultant glass dissolved in dilute hydrochloric acid. After boiling, and standing for several days in a corked flask, the radium emanation was boiled out, collected in a gas-holder, and ultimately transferred to an electroscope. Knowing the normal leak and constant of the electroscope, a measurement of leak sufficed to give the necessary data for the calculation of the equivalent amount of uranium.

Blank experiments were made with the reagents used, and the normal leak was determined at suitable times throughout the investigations. In no case was any appreciable difference observed. Two solutions of each mineral were made, and two estimations of each. Without exception, the results obtained agreed closely.

(b) *Lead.*—Several methods of estimating lead were attempted, but the most constant and reliable results were found to be attained by weighing it as sulphate, and in cases when the quantity of lead present was too small for the gravimetric method, colorimetric estimations were made.

*Gravimetric method.*—Quantities varying up to nearly 100 gm. of the finely powdered mineral were intimately mixed with four or five times as much fusion mixture, and fused in a platinum basin. On allowing the melt to cool completely, the cake could usually be easily separated by treating with boiling water. A second heating and cooling always resulted in a successful separation. The cake was broken up by boiling with water in a beaker. Dilute hydrochloric acid was gently heated in the platinum basin to remove any still adherent portions of the cake. The contents of the basin were then washed into the beaker, and more hydrochloric acid added. The solution thus formed (with a colloidal mass of silica) was evaporated to dryness, and, dilute hydrochloric acid having been added, this was repeated a second time. On again adding dilute acid and heating, the silica was easily filtered off, leaving a clear solution. From the latter lead was precipitated as sulphide, by heating and adding ammonium sulphide. The precipitate was collected on as small a filter paper as possible, dried and ignited. The residue was treated with a little nitric acid, and boiled to convert any reduced lead to nitrate. Sulphuric acid was finally added, and the whole heated until all nitric

\* 'Roy. Soc. Proc.,' A, 1906, p. 473 *et seq.*

acid fumes had ceased. A tiny white precipitate then remained. This was collected on a very small filter, of which the weight of the ash was accurately known, washed with alcohol, dried, ignited, and weighed with the greatest possible accuracy.

*Colorimetric method.\**—Standard solutions containing known quantities of lead, as nitrate, were prepared by dissolving the lead compound in a slightly acidified solution containing ammonium acetate and grape sugar, known as the “diluting solution.”

The lead to be estimated having been concentrated in a nitric acid solution as already described, the latter was evaporated to dryness, or nearly so. The residue was then taken up with a little of the diluting solution. This was treated with a known quantity of well-diluted ammonium sulphide, the liquids being contained in a graduated glass vessel. A brown coloration was produced. One of the standard solutions was similarly treated in an exactly similar vessel. The diluting solution was then added to one vessel or the other until the colours produced in both were indistinguishable, care being taken that the amount of ammonium sulphide in each was proportionate to the respective volume. After a little practice with solutions of known strengths, this could be done with confidence, and concordant results were obtained. Tested by the sulphate methods slightly higher results were given in general.

The colorimetric method obviously assumes the absence of copper and bismuth.

From Vogt's estimates of the average amount of these metals in 100 grm. of rock :—†

	Grm.
Lead .....	0·000 <i>x</i>
Copper .....	0·0000 <i>x</i>
Bismuth .....	0·00000 <i>x</i>

it might be anticipated that the latter two would not have much influence. Tests were, however, applied to detect any very small quantities which might be present. By testing for copper‡ with hydrobromic acid, about 0·00002 grm. was probably the greatest amount indicated. Schneider's test applied for bismuth§ failed to detect that element. To the fourth decimal the amount of lead was therefore unaffected by its non-separation from copper or bismuth.

The smallest amount of lead estimated, viz., 0·0003 grm. in 100 grm. of

\* V. Harcourt, ‘Journ. Chem. Soc.,’ 1910, vol. 97, p. 841.

† ‘Zeit. prakt. Geol.,’ 1898.

‡ ‘Select Methods of Chemical Analysis,’ Crookes, 1905, p. 295.

§ *Ibid.*, 1905, p. 355.

felspar, approaches the limit to which the colorimetric method can be applied quantitatively, although smaller quantities than this can easily be detected.

4. *Experimental Results.*—The results obtained are tabulated below:—

Mineral.	Uranium. Grm. per 100 gm. mineral.	Lead. Grm. per 100 gm. mineral.	Pb/U.
Thorite (1) .....	10·1040	0·4279	0·042
Orangite (1) .....	1·2437	0·0570	0·046
Orangite (2) .....	1·1825	0·0542	0·046
Thorite (2) .....	0·4072	0·0196	0·048
Homelite .....	0·2442	0·0121	0·049
Zircon .....	0·1941	0·0085	0·044
Pyrochlore (1) .....	0·1923	0·0120	0·062
Pyrochlore (2) .....	0·1855	0·0093	0·050
Biotite .....	0·1602	0·0069	0·043
Tritomite .....	0·0631	0·0026	0·041
Freyalite .....	0·0526	0·0028	0·053
Mosandrite .....	0·0432	0·0024	0·056
Eagerine .....	0·0253	0·0015	0·060
Astrophyllite .....	0·0140	0·0007	0·050
Catapleite.....	0·0132	0·0009	0·068
Nepheline.....	0·0010	0·0004	0·400
Felspar .....	0·0006	0·0003	0·500

With the exception of pyrochlore, specimen (1), and astrophyllite, the number of lead estimations varied from two to five. Of the minerals named, only one determination was made, owing to lack of material. It will be noticed that with few exceptions the value of Pb/U increases as the uranium content decreases. This may be due to the possibility of the lead originally present in the magma having a gradually increasing relative importance as the lead generated from uranium decreases in amount. Thus it would seem in the case of nepheline and felspar that the lead so generated is of no importance whatever when compared with that originally present. Such minerals are, of course, valueless in age-estimations, and of the results given here only eight of the first nine will be used for determining the age. Omitting that of pyrochlore (1), since the single rather anomalous determination of lead could not be verified by a second estimation, these results give 0·046 as their mean, and if the uranium percentage be replaced by its approximate time-average the mean becomes 0·045. This gives an age of 370 million years, and is probably the most reliable estimate that can be deduced from the evidence.

5. *Summary of Analyses collected by Boltwood.\**—(a) The analysis of five specimens of uraninite from Glastonbury (Conn.) gives a ratio of Pb/U = 0·041. The minerals occur in a pegmatite associated with a

\* Boltwood, 'Am. Journ. Sci.', 1907, p. 77.

granite intruding Lower Carboniferous strata, and probably itself of Carboniferous age.

(b) Uraninite from Branchville (Conn.) gives four closely agreeing ratios, 0.053. The geological evidence here is similar to that at Glastonbury, with the exception that the intruded strata are of Silurian or Ordovician age.

(c) Material from dykes of pre-Carboniferous age in Carolina gives less consistent results, of which the mean ratio is 0.05.

(d) In Llano Co. (Texas), there occurs a group of metamorphosed sedimentary rocks of early Algonkian age. Into these the Burnet granites are intrusive, and are therefore somewhat younger than the schists and quartzites. The ratio of minerals from these igneous rocks is 0.160.

(e) Another group of minerals from Burnet Co. (Texas) and Douglas Co. (Colorado) gives a ratio of 0.175.

Geological evidence is similar to that of Llano Co., and it is impossible to say whether or not the rocks are older.

(f) The pre-Cambrian rocks of Sweden are divided by Högbom into three main divisions, Jotnian, Jatulian, and Archæan, in order of increasing age. Above the Archæan, but younger than the Jatulian, is a series of igneous massives known as the Sen-archæan granites, and with these are associated the famous uranium-bearing pegmatites of Scandinavia.

In a series of 17 minerals from these pegmatites, taken from all parts of Norway and Sweden, there appear to be two clearly marked groups. One gives a ratio of 0.125 and the other of 0.155. Amongst these rocks geological correlation is very speculative, but it is agreed that there is nothing by which any difference in age could be detected, and provisionally the two groups are regarded geologically as one.

(g) The greatest ratio is given by thorianite from Ceylon, for which  $Pb/U = 0.20$ . Here the only evidence for the pre-Cambrian age of the minerals is derived from the similarity of the rocks to those of the fundamental complex of India. These latter underlie a vast series of sedimentary strata considered to be of pre-Cambrian age.

It should be observed that in calculating the above ratios U represents the time-average, and not the amount actually present. The difference is, however, not great.

6. *Conclusion.*—Evidence has been given to prove that the ratio  $Pb/U$  is nearly constant for minerals of the same age, the slight variability being what theoretically one would anticipate.

For minerals of increasing geological age the value of  $Pb/U$  also increases, as the following table clearly shows :—

Geological period.	Pb/U.	Millions of years.
Carboniferous .....	0·041	340
Devonian .....	0·045	370
Pre-carboniferous .....	0·050	410
Silurian or Ordovician .....	0·053	430
Pre-Cambrian—		
<i>a.</i> Sweden .....	0·125	1025
	0·155	1270
<i>b.</i> United States .....	0·160	1310
	0·175	1435
<i>c.</i> Ceylon .....	0·20	1640

Wherever the geological evidence is clear, it is in agreement with that derived from lead as an index of age. Where it is obscure, as, for example, in connection with the pre-Cambrian rocks, to correlate which is an almost hopeless task, the evidence does not, at least, contradict the ages put forward. Indeed, it may confidently be hoped that this very method may in turn be applied to help the geologist in his most difficult task, that of unravelling the mystery of the oldest rocks of the earth's crust; and, further, it is to be hoped that by the careful study of igneous complexes, data will be collected from which it will be possible to graduate the geological column with an ever-increasingly accurate time scale.

In conclusion, I wish to express my thanks to those gentlemen who in any way have helped to make this investigation possible. I am indebted to Profs. Sir T. H. Holland, Brögger, and Högbom, and to the Director of the United States Geological Survey, for information regarding the geological position of many of the occurrences cited in §5; and to Dr. Prior for his permission to make preliminary electroscopic tests of several minerals in the collection of the Natural History Museum. Finally, I owe my best thanks to Prof. Strutt, at whose suggestion the work was attempted, for his ever-ready help and criticism, and for his kindness in obtaining for me the suite of minerals and allowing me the use of apparatus in their investigation.

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