THE HELIUM CONTENTS AND THE AGES OF JAPANESE RADIOACTIVE MINERALS OCCURRING IN ISHIKAWA DISTRICT.

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It is well known that granted certain conditions of suitability, it is possible to calculate the age of a primary radioactive mineral from its contents of uranium, thorium and one of their disintegration end-products, i. e., lead or helium.

There occur in Ishikawa District, Japan, several kinds of radioactive minerals—ishikawaite,[1] samarskite, xenotime and monazite. A series of experiments has been undertaken to determine their contents of helium, from which the authors have calculated their ages. Determining the amount of lead in the ishikawaite, the authors have also estimated its maximum age[2] and compared it with its minimum one calculated from the helium content.

Experimental.

The apparatus employed for the determination of helium is illustrated in Fig. 1. It is similar with that used by the authors for the measurement of helium in the natural gases of Japan,[3] but the whole apparatus is constructed in a smaller size with some suitable modifications. A and B in Fig. 1 show the silica bulbs in which a sample of mineral is heated for the extraction of helium. A is used for dry heating and B for wet treatment of a sample.

As there is a fear of causing an appreciable error in the measurement of a small quantity of helium, if helium is absorbed by cocoanut charcoal cooled by liquid air even at reduced pressure, so the authors have made a preliminary experiment to determine the amount of helium absorbed by the charcoal in the bulb D.

Heating the bulb D to 300°C. by electric furnace, the whole apparatus is exhausted to a vacuum by an oil pump and further by the Töpler's pump F. After cooling of the bulb D, C and D are immersed in liquid air and a definite amount of helium is then introduced into the apparatus from the burette G. The experiment must be carried out with the same care as was

(1) A new kind of uranium mineral was found by Prof. Y. Shibata and named "ishikawaite". [*J. Chem. Soc. Japan*, **43** (1922), 648].

(2) E. Rutherford, "Radioactive Substances and their Radiations", (1913), p. 562, 599.

(3) *J. Chem. Soc. Japan*, **47** (1926), 13 & 452; *Report of the Aeronautical Research Institute, Tokyo Imperial University*, Vol. 1, No. 13 (1926).

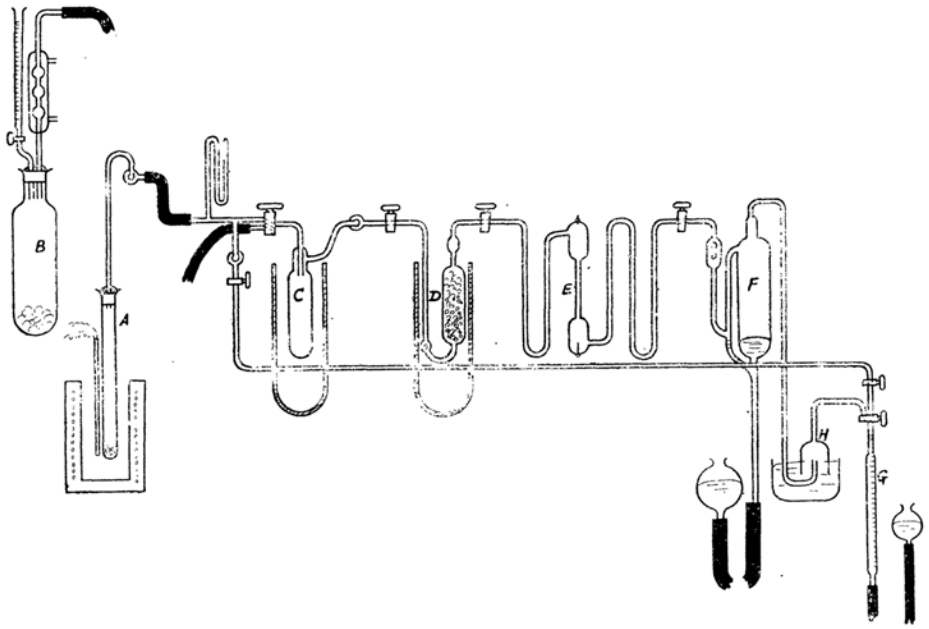


Fig. 1.

taken in the case of analysis of natural gases.[1] Lastly, the helium is drawn over into the adapter tube H by the Töpler's pump F. And as its quantity is measured by the burette G, the amount of helium absorbed by the charcoal in the bulb D can be calculated. Mc Lean[2] observed in his experiment that the amount of helium absorbed by charcoal was so small that it was nearly independent on the quantities of helium introduced into the charcoal bulb. The result of the authors' experiment shown in Table 1, gives the same conclusion.

TABLE 1.

Reaction bulb	Helium introduced (c.c.)	Helium absorbed (c.c.)	Helium absorbed per gr. of charcoal (c.c.)
A (80 c.c.)	0.501	0.041	0.0018
	2.317	0.048	0.0021
	4.891	0.050	0.0022
B (400 c.c.)	0.565	0.038	0.0017
	2.293	0.049	0.0022
	4.812	0.056	0.0025

(1) loc. cit.

(2) *Trans. Roy. Soc. Canada*, **12**, III (1918), 79.

Therefore, in the experiment for the determination of helium present in a radioactive sample, a small amount of helium is previously introduced into the apparatus and after a short time the apparatus is evacuated untill no spark can be passed through the Plücker's tube E. And then, the sample being heated with or without a reacting agent, the helium is evolved and measured in the same manner as above. Powdered samples are used in all the experiments.

Helium in the Ishikawaite. The most radioactive mineral which, like the other minerals, has occurred in Ishikawa District accompanying smoky quartz, microline and biotite in pegmatite layers, has been identified by means of chemical analysis with a mineral named "ishikawaite". It contains 20.86% uranium and 7.5% rare earth elements, possessing a specific gravity 6.3.

The amounts of helium liberated when the sample is heated at 1000°C. and when it is fused with acid potassium sulphate (one part of the sample and 8 parts $KHSO_4$) at 700°C. are given in Table 2, showing that the both methods give a concordant value.

TABLE 2.

Amount of mineral used (gr.)	Method of treatment	Heating temperature (°C.)	Heating duration (hours)	Helium evolved (c.c. at N.T.P.)	Helium per gr. of mineral (c.c.)
2.0013	Mere heating	1000°	2	3.551	1.77
2.0020	One part of the sample is fused with 8 parts of $KHSO_4$.	700°	7	3.483	1.74

TABLE 3.

Amount of mineral used (gr.)	Heating duration at 700°C. (hours)	Helium evolved (c.c.)	Helium evolved per gr. of sample (c.c.)
2.0021	½	3.229	1.613
1.9999	1	3.346	1.673
1.0015	1½	1.701	1.698
2.0005	2	3.448	1.723
2.0000	4	3.465	1.733
2.0020	8	3.483	1.740

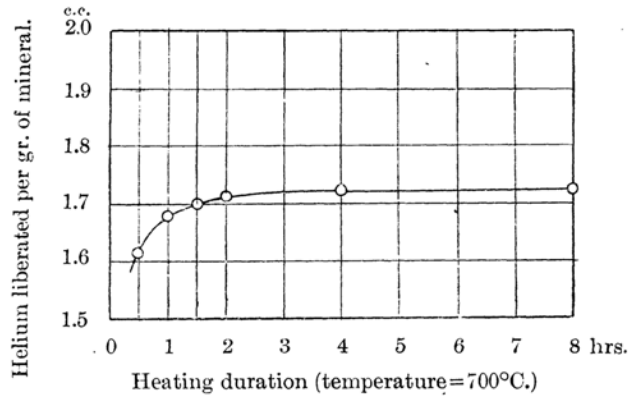


Fig. 2.

Table 3 and Fig. 2 show the effect of heating duration on the liberation of helium when the sample is fused at 700°C. with the same amount of $KHSO_4$ as itself. It is seen that the gas is emitted almost completely after four hours' fusing. If the heating temperature is raised more than 700°C., the rate of liberation of helium increases. This is evident from the results shown in Fig. 3 and Table 4. For the deficiency of the pure sample of ishikawaite, it has been obliged to use a sample somewhat mixed with columbite in this case. The sample contains 14.26% UO_2. Curve I gives the amounts of helium emitted by mere heating of the sample for two hours at various temperatures. On red heat (700–800°C.) the gas in the mineral is liberated nearly by one half but at a temperature higher than 900°C. it is

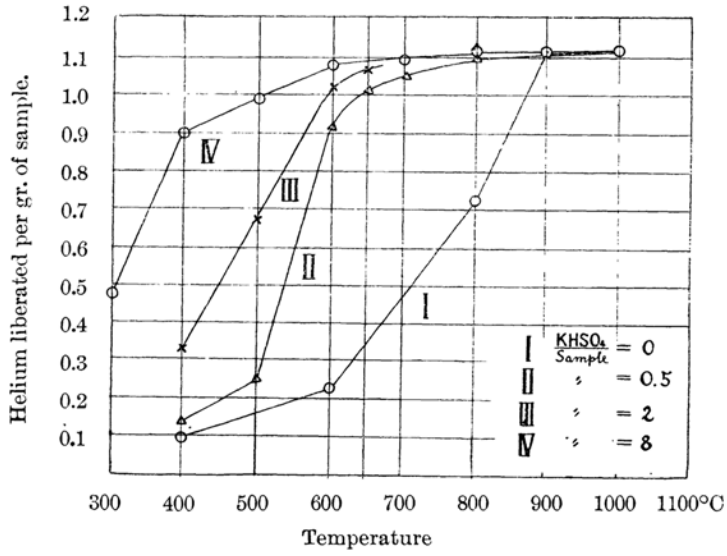


Fig. 3.

given off almost completely. The other curves (II, III & IV) show the quantities of helium evolved when the mineral is fused with $KHSO_4$ at various temperatures, each curve corresponding to each different amount of the fusing agent as noted in the figure. The more the fusing agent is used, the easier the helium in the mineral comes off at any temperature below 900°C. But at **1000°C.** the gas in the mineral is liberated completely, independently of the amounts of the fusing agent.

TABLE 4.

Amount of fusing agent	Fusion temp. (°C.)	Amount of mineral used (gr.)	Helium evolved (c.c.)	Helium per gr. of mineral (c.c.)
Mere heating without fusing agent	400	1.4992	0.144	0.096
	600	1.9984	0.472	0.236
	800	1.5011	1.099	0.732
	900	1.3512	1.499	1.109
	1000	1.9992	2.238	1.119
$\frac{KHSO_4}{\text{mineral}} = \frac{1}{2}$	200	1.0003	0	0
	400	1.0003	0.134	0.134
	500	1.0018	0.250	0.250
	600	1.0013	0.919	0.918
	650	1.0001	1.017	1.017
	700	1.0020	1.051	1.049
	800	1.0002	1.100	1.100
	1000	0.9993	1.121	1.122
$\frac{KHSO_4}{\text{mineral}} = 2$	400	1.0013	0.337	0.337
	500	1.0007	0.653	0.653
	600	1.0003	1.050	1.050
	650	1.0003	1.070	1.070
$\frac{KHSO_4}{\text{mineral}} = 8$	200	0.9995	0	0
	300	0.9997	0.480	0.480
	400	0.5004	0.448	0.897
	500	0.5018	0.494	0.984
	600	0.5010	0.542	1.082
	700	0.5003	0.548	1.095
	800	0.5005	0.565	1.129
	1000	0.4994	0.563	1.127

Helium in the Monazite[1] from Ishikawa. The result of experiments on the monazite is shown in Table 5. When the mineral is heated at

(1) J. Sasaki determined the amount of helium which was liberated by this mineral on red heat, and assuming that the quantity was half the whole content of helium, he calculated the age of the mineral (this journal, 1 (1926), 253).

1000°C., it gives off nearly the whole of its helium within several hours, what is found to agree with the result of D.O. Wood's experiment.(1) The helium in the mineral is also liberated almost completely when it is heated with sulphuric acid at a lower temperature for a longer time. Table 6 and Fig. 4 give the temperature effect on the liberation of helium. Five hours' heating at 600°C. makes the sample to give off not more than half the helium present in the mineral, but at a temperature above 800°C. the whole of the gas is emitted for the time.

TABLE 5.

Amount of mineral used (gr.)	Method of treatment	Helium evolved (c.c. at N.T.P.)	Helium per gr. of mineral (c.c.)
4.9991	Heating at 800°C. for 5 hours.	1.115	0.223
3.1254	„	0.725	0.232
3.6709	Heating at 1000°C. for 5 hours.	0.903	0.246
9.9983	Heating at 320°C. with conc. H_2SO_4 for 3 hours.	2.109	0.211

TABLE 6.

Amount of monazite used (gr.)	Heating temperature (°C.)	Heating duration (hours)	Helium evolved (c.c. at N.T.P.)	Helium per gr. of mineral (c.c.)
4.9970	400°	5	0.140	0.028
4.9953	600	„	0.734	0.147
3.1254	800	„	0.725	0.232
3.6709	1000	„	0.903	0.246

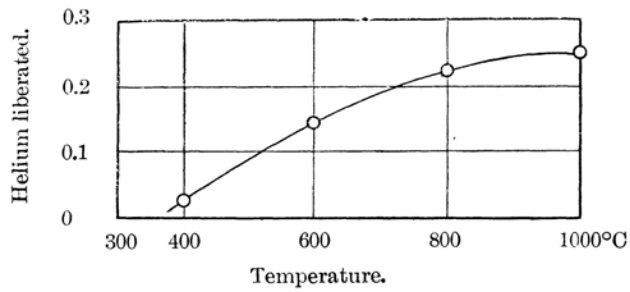


Fig. 4.

(1) *Proc. Roy. Soc. London*, A 84 (1911), 70.

Helium in the Samarskite and the Monazite from Ishikawa. For the liberation of helium in these two minerals, only the heating method is used for the deficiency of the samples. But as the minerals are heated at 1000°C., it may be reasonably acknowledged in view of the results obtained in the cases of ishikawaite and monazite, that each of the minerals loses the whole of its helium.

TABLE 7.

Kind of mineral	Amount used (gr.)	Method of treatment	Helium evolved (c.c.)	Helium per gr. of mineral (c.c.)
Samarskite	3.0011	Heating at 1000°C. for 3 hours.	4.263	1.420
Xenotime	3.2812	Heating at 1000°C. for 2 hours.	0.083	0.025

Calculation of the Ages of the Radioactive Minerals.

The age of a primary radioactive mineral can be calculated from its contents of uranium, thorium and one of their disintegration products, helium or lead. The contents of uranium and thorium in the ishikawaite have been determined by the method of Prof. Y. Shibata,[1] and the amount of lead in the same sample has been measured according to the analytical process outlined in the Table 8. The analysis gives the following result:

Uranium, 20.86% (23.65% as UO_2).

Thorium, nil.

Lead, 0.36%.

For the calculation of the ages of the samarskite and the monazite, the data of Profs. Y. Shibata and K. Kimura[2] on the uranium and thorium contents of the minerals are used.

Samarskite: uranium, 14.87%; thorium, nil.

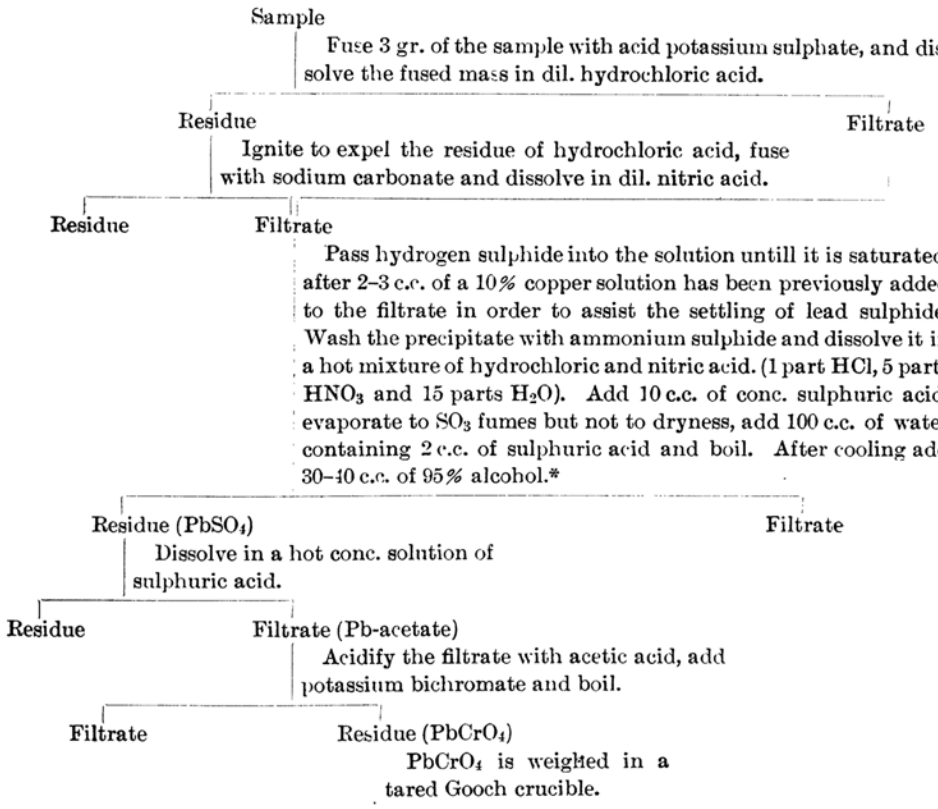
Monazite: uranium, 0.37%; thorium, 8.50%.

(1) *J. Chem. Soc. Japan*, **43** (1922) 307.

(2) *J. Chem. Soc. Japan*, **43** (1922) 301; **42** (1921), 961.

TABLE 8.

Method of the determination of lead in ishikawaite.



* see W. Scott, "Standard Method of Chemical Analysis". Vol. 1, p. 208.

If (U), (Th) and (Pb) denote the percentage contents in a mineral of uranium, thorium and lead of radioactive origin respectively, the age in millions of years of mineral is given approximately by the formula,

$$\text{Age} = \frac{(Pb)}{(U)+k(Th)}\ C,$$

where k and C are constants, the most trustworthy values of which have been given by A. Holmes and W. Lawson[1] to be: $k=0.38$ and $C=7.400$. The correction may be made for the wearing out of uranium and thorium during the life-time of the mineral, but it can be neglected in the case of relatively young minerals as those from Ishikawa.

(1) *Am. J. Science*, 76 (1927), 327.

Another expression for the age of a mineral by the helium method is given by A. Holmes and W. Lawson, thus

$$\text{Age} = \frac{(He)}{(U)+0.29\,(Th)} \times 8.5 \text{ million years},$$

where (U) and (Th) denote the percentage contents of the uranium and the thorium in the mineral respectively, and (He), the volume in c.c. of helium at N.T.P. in 100 gr. of the mineral.

According to these formulas the ages of the minerals occurring in Ishikawa have been calculated from the data given in preceding pages.

$$\text{Age of the ishikawaite} = \frac{(He)}{(U)+0.29\,(Te)} \times 8.5$$

$$= \frac{177.5}{20.85} \times 8.5 = 72.3 \text{ million years}$$

(by the helium method)

$$= \frac{(Pb)}{(U)+0.38\,(Th)} \times 7{,}400$$

$$= \frac{0.36}{20.85} \times 7{,}400 = 127 \text{ million years}$$

(by the lead method).

$$\text{Age of the samarskite} = \frac{142.1}{14.87} \times 8.5 = 81.2 \text{ million years.}$$

$$\text{Age of the monazite} = \frac{24.6}{0.37+0.29\times 8.5} \times 8.5 = 73.9 \text{ million years.}$$

It is to be naturally expected that the age calculated with lead as an index is greater than the age calculated from the amount of helium present in the mineral. Such is shown in the case of the ishikawaite.[1]

The result of calculation shows that these three minerals from Ishikawa belong to almost a same geological age which must be considered to be Jurrassic or early Crataceous. This consideration is justified by the direct evidence that the pegmatites in which these minerals occur are regarded to belong to the Mesozoic Group.

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(1) Y. Uzumasa gives 29.2 million years as the age of the ishikawaite, determining the amount of lead in the mineral by a colorimetric method, but his value appears to be too small. (see *J. Chem. Soc. Japan*, **48** (1927), 406).