THE RADIOACTIVE CONSTITUENTS OF HOKUTOLITES AND OTHER MINERALS IN JAPAN.

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The radioactivity of the hokutolite from the Hokuto hot-spring in Taiwan has been studied by several investigators since its discovery in 1906 by Y. Okamoto. M. Hayakawa and T. Nakano(1) pointed out the presence of ionium, radium and polonium as its radioactive constituents, examining merely the characteristics of the decay curves of radioactivity shown by the particular fractions separated by chemical processes. On the hokutolite from the Shibukuro hot-spring in Akita Prefecture, R. Ohashi(2) determined its radium-content, and recently I. Suganuma(3) proved qualitatively that the radioactive constituents of this mineral consists of radium, polonium and thorium. Majority of these previous investigations have, however, been wholly deficient in the quantitative examination of the radioactive constituents, hence in the present work the author has determined the amounts of radium and thorium in the above mentioned hokutolites as well as those in the allanite from Shirakawa near Kyoto and the radium-content of the xenotime from Ishikawa, Fukushima Prefecture, by the accurate measurements of the emanations given out from these minerals.

Samples Used for Analyses. *Hokutolite from the hot-spring of Hokuto, Taiwan.*—This mineral occurs as a crystalline crust which grows on the bottom of the river, where runs hot-spring water gushed out. Thickness

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(1) M. Hayakawa and T. Nakano, *Z. Anorg. Chem.*, **78** (1912), 183.

(2) R. Ohashi, *Min. Mag.*, **19** (1920), 73; *J. Chem. Soc.*, **118** (1920), Abs. ii, 550.

(3) I. Suganuma, this Bulletin, **3** (1928), 69.

7—8 mm. Yellowish brown and translucent. This crystalline crust was carefully taken from its mother-rock and analyzed.

Hokutolite from the hot-spring of Shibukuro, Akita Prefecture.—This specimen is also a thick crystalline crust similarly produced as that from Hokuto, and thicker than the latter. On the surface of this crust, there are recognized some minute crystals and the fracture shows a zonal structure consisting alternately of brown and white ingredients. An average portion of these ingredients was taken for analysis.

Allanite from Shirakawa, Kyoto Prefecture.—The allanite is a black prismatic crystal taken out from the granite occurring in this locality. The crystals measure about 5—6 mm. in length and 1—2 mm. in diameter.

Xenotime from Ishikawa, Fukushima Prefecture.—Xenotime occurs in this quarter usually intermingled with zircon, the former always developing around the crystal of the latter. A special form of aggregate consisting of such intermingled crystals is sometimes called "Kikukwa-seki" in this district. It is almost impossible to obtain pure xenotime entirely free from zircon, and so the lumps of such intermingled crystals were employed for analysis, a special care having been taken in the disintegration process, so as not to decompose the zircon, of which will be described latter.

Treatment of Minerals. *Hokutolite.*—The finely ground sample was fused with a quantity of fusing mixture, and the melt was extracted with water and filtered. For the extraction of emanations, the solution obtained by dissolving the residue in nitric acid was called the "first solution," and the filtrate acidified with nitric acid, the "second solution."

Allanite.—The sample was pulverized and fused with fusing mixture. The melt was lixiviated with water containing hydrochloric acid and filtered. The residue was very small in quantity. In the filtrate, the silica was removed by usual method and the solution thus obtained was called the "first solution". The insoluble residue was then fused with potassium pyrosulphate, and brought to a solution being dissolved in water acidified with sulphuric acid. The clear solution thus obtained was chiefly used for the determination of thorium, being called the "second solution".

Xenotime.—The finely powdered mineral was left for more than a month to let the radium emanation come into equilibrium. The sample, thus prepared, was directly employed for the estimation of radium emanation, so that a quantity of the sample was transferred into a large test-tube made of quartz-glass and an excess of concentrated sulphuric acid was then added. Having been boiled this mixture over a moving flame, all the radium emanation contained in the sample was evolved. The latter was collected by a suitable means in an emanation reservoir and then introduced into an electroscope for the measurement. There is no doubt in this treatment, about the fact that the xenotime alone is completely decomposed whilst the zircon may hardly be attacked. It may, therefore, be safely asserted that the emanation measured in this case is wholly derived from the xenotime.

Determination of Radium. For the measurement of radium, the electroscope and accessory apparatuses formerly deviced by F. Soddy⁽¹⁾ were employed. Each solution for the examination was kept in a sealed emanation bottle under a little reduced pressure. After having been left for more than a month in this sealed state, the solution was used for the determination. The electroscope was calibrated by the radium standard solutions prepared from the Cornish pitchblende, which was previously analyzed by Dr. S. Iimori and determined the amount of uranium as to be 44.37% U_3O_8, accordingly 1.28×10^{-5}% radium.

Using the above standards, the constant of the electroscope was determined as follows:—

Standard solution	Radium-Content (gr.)	Activity (div./min.)	Constant of Electroscope (10^{-12} gr. Ra per div./min.)
I	1.73×10^{-10}	5.77	30.0
II	,,	5.71	30.3
			mean, 30.2

The results are shown in tabular form in the rear.

Determination of Thorium. The determination of thorium was carried out by the constant current method.⁽²⁾ According to G. H. Cartledge,⁽³⁾ the degree of accuracy of this method is said to be about 1.5%. Before the measurement, the radium emanation in the sample solution was always completely expelled by boiling and letting air bubble through the solution. A steady current of air from a Mariotte's bottle being then bubbled in the sample solution, the thorium emanation was continuously conveyed into the emanation chamber of the electroscope through a drying tube filled with calcium chloride. The readings were taken when the rate of discharge in the electroscope had come to constant under a steady flow of air through the apparatus.

As the standard of thorium, the thorianite from Ceylon was used. The amount of thorium of this mineral was previously determined by gravimetric analysis to be 52.92% ThO_2. A definite quantity of the thorianite,

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(1) F. Soddy, *Phil. Mag.*, (6) **18** (1909), 846.
(2) R. J. Strutt, *Proc. Roy. Soc.*, A, **76** (1905), 88; J. Joly, *Phil. Mag.*, (6) **17** (1909), 760.
(3) G. H. Cartledge, *J. Am. Chem. Soc.*, **41** (1919), 42.

viz. in the experiment 0.1199 gr. was dissolved in concentrated nitric acid and diluted to about 150 c.c. with water, small insoluble parts, which did not contain any radiothorium and thorium X, having been filtered off. In this method of measurement, it is important to keep the standard solution and sample solutions in the same comparable condition throughout the whole experiment, which is, however, rather difficult in practice. Hence the calibration of the standard solution was made every time as soon as the measurement of a sample solution was finished, as will be seen in the results given in Table 2.

Experimental Results. The results obtained in the measurements of the amounts of radium and thorium in the minerals are given in the following tables.

Table 1. Radium-Content.

Mineral	Sample taken (gr.)		Activity (div./min.)	Radium-Content			Uranium-content (as U_3O_8) (%)
				of each soln. (gr.)	Total		
					(gr.)	(%)	
Hokutolite (Hokuto, Taiwan)	(I) 1.0194	The 1st soln.	58.9	1778×10^{-12}	1.78×10^{-9}	1.75×10^{-7}	—
		The 2nd soln.	0.03	0.9×10^{-12}			
	(II) 1.0211	The 1st soln.	57.3	1740×10^{-12}	1.74×10^{-9}	1.70×10^{-7}	—
		The 2nd soln.	— *	—			
						mean, 1.73×10^{-7}	
Hokutolite (Shibukuro, Akita Pref.)	1.1487	The 1st soln.	46.3	1398×10^{-12}	1.40×10^{-9}	1.22×10^{-7}	—
		The 2nd soln.	0.03	0.9×10^{-12}			
Allanite (Shirakawa, Kyoto Pref.)	0.8112	The 1st soln.	1.11	33.5×10^{-12}	3.95×10^{-11}	4.87×10^{-9}	0.017
		The 2nd soln.	0.20	6.0×10^{-12}			
Xenotime (Ishikawa, Fukushima Pref.)	(I) 0.7157		168.1	—	5.08×10^{-9}	7.09×10^{-7}	
	(II) 0.1228		27.8	—	0.839×10^{-9}	6.83×10^{-7}	
	(III) 0.1438		33.5	—	1.01×10^{-9}	7.03×10^{-7}	
						mean, 6.98×10^{-7}	2.42

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*The measurement was omitted, since the activity of the second solution was very little as seen in the case of the sample (I).

In the above table, the amount of uranium was calculated from that of radium, taking the equilibrium-ratio of radium to uranium to be 3.4×10^{-7}.

Table 2. Thorium-Content.

Mineral	Sample taken (gr.)		Constant of Electroscope (gr. ThO_2 per div./hr.)	Activity (div./hr.)	Thorium-Content (as ThO_2)		
					of each soln. (gr.)	Total	
						(gr.)	(%)
Hokutolite (Hokuto, Taiwan)	1.0194	The 1st soln.	3.54×10^{-4}	0.4	1.4×10^{-4}	2.1×10^{-4}	0.02
		The 2nd soln.	,,	0.2	0.7×10^{-4}		
Hokutolite (Shibukuro, Akita Pref.)	1.1487	The 1st soln.	3.56×10^{-4}	0.3	1.1×10^{-4}	1.1×10^{-4}	0.01
		The 2nd soln.	—	— **	—		
Allanite (Shirakawa, Kyoto Pref.)	0.8112	The 1st soln.	3.78×10^{-4}	14.5	0.0055	0.0085	1.05
		The 2nd soln.	3.41×10^{-4}	8.8	0.0030		

Summary.

As to the uranium in hokutolite, there is no analytical evidence, hitherto, of its presence in this mineral, and it is thought quite useless to calculate it from the amount of radium, as the mineral is obviously of the secondary nature.

The radium- and thorium-contents of the two kinds of hokutolites mentioned above are respectively of the same order and quite similar. The comparatively large content of radium, however, in comparison with the poorer content of thorium shows that the radioactivity of this mineral is mainly ascribed to radium and its disintegrating products and very little to the members of thorium-series.

It is seen that the allanite from Shirakawa, Kyoto Prefecture contains 1.05% ThO_2 and 0.017% U_3O_8.

The uranium-content of the xenotime-portion of the xenotime-zircon from Ishikawa was determined to be 2.42% U_3O_8. According to K. Kimura(1), the average amount of uranium in the "Kikukwa-seki" is said as being

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**It has shown almost no activity.

(1) K. Kimura, *Japan. J. Chem.*, **2** (1925), 73.

1.92% UO_2. These results indicate that the amount of uranium in the zircon-portion of the latter mineral is probably less than that in the xenotime portion.

In conclusion, the author wishes to express his hearty thanks to Dr. S. Iimori for his kind direction during the course of this experiment.

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