ON THE CONSTITUENTS AND GENESIS OF A FEW MINERALS PRODUCED FROM HOT SPRINGS AND THEIR VICINITIES IN JAPAN[1]. I. THE AKITA HOKUTOLITE.

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The Constituents and Genesis of the Akita Hokutolite Produced from a Sulphurous Hot Spring called Shikayu in Akita Prefecture. A heavy crystalline mineral produced from a sulphurous spring in Akita-ken, a province of Japan, is very similar in its appearance and properties to hokutolite from the Hokuto Spring in Taiwan i. e. Formosa.[2] Some mineralogists of this country supposed that the former mineral is of the same kind as the latter, but this not being proved by any accurate experiments, the author analysed and examined the former mineral, and has obtained the result that it is of the same kind as hokutolite. Therefore the author thinks that the mineral can properly be called the *Akita hokutolite.* The chief constituents of the Akita hokutolite are $BaSO_4$ and $PbSO_4$, and the mineral consists of the isomorphous mixture of the above constituents just as the Taiwan hokutolite does, but the former differs from the latter in the following points:—

(1) The different samples of the Akita hokutolite vary in a wide range in their compositions i. e. the ratios of $BaSO_4$ and $PbSO_4$ contained in them,

(1) Read before the Chemical Society of Japan, July 11, 1922.

(2) Okamoto, *J. Geol. Soc. Tokyo,* 18 (1911), 19; *Beitr. Mineral. Japan,* 4 (1912), 178; Hayakawa and Nakano, *Z. anorg. Chem*, 78 (1912), 183; Richards and Sameshima, *J. Am. Chem. Soc.*, 42 (1920), 928.

while the composition of the Taiwan hokutolite is approximately constant.

(2) Generally, $BaSO_4$ predominates in the former mineral than in the latter, and sometimes is nearly equal to a mineral barite.

(3) The Taiwan hokutolite is always of brown colour, while the Akita hokutolite is sometimes of light yellow or even white, besides the ordinary kind of brown colour.

(4) As a remarkable difference, the accompanying rare elements of the Akita hokutolite are much greater in kinds than those reported on the Taiwan hokutolite, especially, the radioactivity of the mineral is not only ascrived to the radio-active elements of radium series but to the radio-active elements of thorium series, because the presence of thorium and its active deposits has been proved by the chemical analysis and the radioactive experiments.

(5) The commonest kind of the Akita hokutolite is composed from a great number of small rhombic brownish crystals as the Taiwan hokutolite, but the former contains thin white layers in regular intervals i. e. a zonal structure of the two layers of brown and white, while such two different layers are not clearly perceived in the latter mineral.

The author separated the two layers of the Akita hokutolite from each other and analysed each layer in order to find out the difference between the compositions of the two layers.

The results of the analysis show that in the white layer $BaSO_4$ is much greater than in the brownish layer, and also SiO_2 is somewhat greater, while in the brownish layer predominate PbO and FeO as $PbSO_4$ and probably PbS_5O_6, x FeS_5O_6. The author ascrives the brownish colour of the mineral to pentathionate of Pb and Fe from several experimental facts.

The ordinary metallic elements contained as impurities in the Akita hokutolite are Sr, Ca, Mg of Ba group with Al and Fe; and further the presence of the rare metallic elements such as Ti, Zr, Th, Ce, La, Pd and Nd, and Ra, Rn, Po of U series has been determined qualitatively (but some quantitatively) in the mineral.

Among these, the presence of Th has been ascertained by the analytical results and by tracing the decay curve of active deposits of Th emanation, but radium accompanying Ba salts in a very minute quantity is proved only by the radio activity of the solid salts and by determining half period of radium emanation evolved from the solution of those salts.

As to uranium, the mother element of radium, the author could only find a trace of it by the colour reaction with $K_4Fe(CN)_6$, but polonium, one of the transformation products of radium, could easily be detected by its characteristic chemical reactions and by plotting the decay curve particular to the metallic film of Po deposition on the bismuth plate.

Therefore, the radio activity of the Akita hokutolite is due to the several radio active elements belonging to radium series and thorium series.

In regard to the genesis of the Akita hokutolite, the author has found the facts that it is deposited only on the rock surface which is covered or washed by the spring water cooled to the temperature of 40°C. and that this temperature highly favours the growth of Cyanophyceae, and further that the gelatinous matter contained in these Cyanophyceae causes the coagulation of silicic acid hydrosol from the acidic solution containing aluminium ion just as the ordinary gelatine or albumen does.

Thus the author has come to assume that the components of the hokutolite come gradually to coat the rock surface by the aid of the silicic acid hydrogel.

In regard to the zonal structure of the hokutolite i. e. white and brown layers, the author considers that the white layer, which is mostly composed of matters with very insoluble properties such as $BaSO_4$, is formed by a current of the strongest acidity and also of the highest temperature.

Such an acidity and temperature can exist only with the smallest supply of the river water in the coldest season.

Pentathionate and sulphide of lead and iron are almost dissolved by such a hot acidic current. Thus we have a white layer and a white deposition. Sometimes in this season, the upper dried part of the rock above the surface of the current, exposes Cyanophyceae to the coldest atmospheric air and destroys the vegetable constitutions, leaving behind a gelatinous or slimy matter. The rock surface naturally absorbs the splashes of the river water and coagulates silicic acid hydrosol contained in them.

This conclusion on the formation of the white layer in the coldest season is pretty well confirmed by the surfaces of those samples which the author collected in that season.

In regard to the brown layer of the hokutolite, the gelatinous matter produced by the natural metabolysm of Cyanophyceae first coagulates silicic hydrosol and gradually adsorbs more and more of those brown components insoluble in the warm dilute acid.

Besides, the author observes about some other specimens that Cyanophyceae are totally destroyed by the cold flood of melted snow in the spring season. In most of these cases, the gelatinous matter contained, cooperates with the aluminium ion in the river current in coagulating the silicic hydrosol forming a muddy brown deposition. In either of these cases, the brown layer contains a comparatively larger proportion of lead and iron compounds soluble in acid water at a higher temperature than 40°C.

In fact the sample of the Akita hokutolite collected in the lowest part of the current contains the largest proportion of lead, but that collected in the vicinity of the source of the spring the smallest proportion of lead and iron as shown by the Table 2.

The latter sample, which is very near to barite in its composition, appears to have been deposited upon rocks exposed out of the river surface, the hot water splashing out energetically from a certain spring, having been cooled down. It is probable that these depositions have been cemented by the colloidal silicic acid precipitated first, because when the hot water of the spring source is collected in a beaker and allowed to cool for a while, the clear liquid gradually becomes cloudy and precipitates colloidal silicic acid hydrogel as has been observed by the author.

The following tables show the compositions of the white and brown layers in the Akita hokutolite compared (Table 1), and the compositions of the samples collected in the vicinity of the spring source and at the lowest part of the river current (Table 2), as well as the composition of the spring source itself (Table 3).

TABLE 1.

Compositions of the white and brown layers of the Akita hokutolite:

Component	White layer	Brown layer	Component	White layer	Brown layer
PbO	6.45	9.72	K_2O	0	0
BaO	55.33	53.80	Na_2O	—	—
SrO	0.11	0.08	SiO_2	4.61	2.53
CaO	0.34	0.32	SO_3	31.43	32.19
MgO	0.25	0.25	As_2O_5	(0.01)	—
Fe_2O_3(CeO_2, ThO_2, etc.)	0.43	0.54	NH_4Cl	—	(0.02)
Al_2O_3	0.52	0.47	total	99.48 %	99.92 %

TABLE 2.

Compositions of the samples collected in the vicinity of the spring source and at the lowest part of the hot river current:

Component	Sample at the upper part of the spring.	Sample at the lowest part of the river.	Component	Sample at the upper part of the spring.	Sample at the lowest part of the river.
BaO	62.18	48.47	MgO	—	0.20
PbO	4.61	15.04	SiO_2	0.44	3.28
Fe_2O_3 } Al_2O_3 }	0.26	0.52	SO_3	32.49	30.31
CaO	—	0.38	total	99.98 %	98.20 %

TABLE 3.

Composition of the spring source called Akita Shikayu.
(1000 parts taken ; temperature of the spring 97°C., strong acid.)

$BaSO_4$	0.0011	$NaCl$	0.1121
$PbSO_4$	0.0009	NH_4Cl	0.0003
$FeSO_4$	0.1832	HCl	2.5497
$Al_2(SO_4)_3$	0.8610	H_2SO_4	0.4247
$CaCl_2$	0.0033	H_2SiO_3	0.3436
$MgCl_2$	0.0581	H_3BO_3	tr.
$AsCl_3$	0.0027	$ZrCl_4$	tr.
KCl	0.0752		

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