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On the Mineral containing Rare Elements (Part 10) Allanite found in Angaku Mine, Kokaido, Korea

By

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The Angaku Mine lies about 19 km to the north of the Shinsen railway station on the Kokai branch of the Keijyo-Shigishu line. Pre-Cambrian granite gneiss and Cretaceous biotite granite and a large number of aplites, pegmatites and quartz veins, probably derived from the late biotite granite intrusion, are distributed in this field. These veins are, however, mostly located in the granite gneiss area and so their croppings are quite restricted with its shistosity (see Fig. 1). Allanite under consideration is contained in some pegmatites or aplites, accompanied with several other minerals, such as garnet, hornblende, tremolite and zircon. On the occurence of allanite, we are able to present the following general conclusions from our field observations which may make an important basis of genetical consideration. (1) Allanite is contained in the pegmatite or aplite vein, but never in the quartz vein. (2) Generally the aplite or pegmatite veins, located in biotite granite, do not contain allanite. In rare cases, however, we can find its small crystals aggregated with biotite only around the xenolith of the granite gneiss. (3) Associated with both biotite and garnet, it is usually shown in small crystal form, while in the case of allanite associated with biotite only, it is shown in

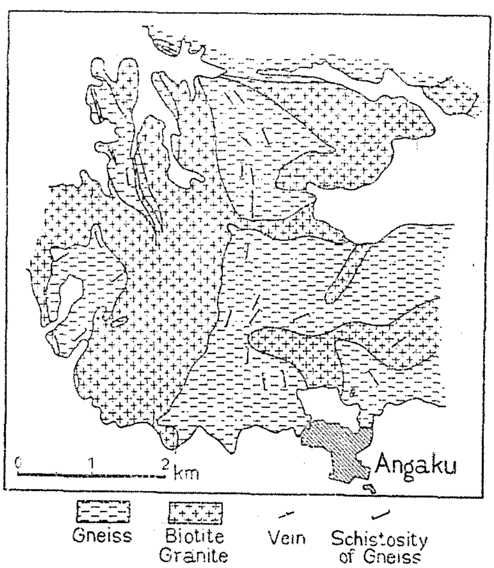

Fig. 1

large crystal form. There is no case in which it is associated with garnet only. (4) Allanite is contained not only in the aplite or pegmatite veins, but also in granite gneiss, in contact with the vein. In this case, it appears generally in large masses, accompanied with biotite in large crystal form.

Physical Properties : $H = 5 - 6$ The color is black; The streak is brown, and each fresh fracture has a somewhat resinous luster. Specific gravity was determined by the pycnometer method with two specimens; one that is associated with both biotite and garnet (1) and the other with hornblende, tremolite, quartz, zircon and titanite (2). Under the microscope, the latter is seen to have some enclosure of minute crystals. On account of this fact, special caution was taken to select the sample used in this determination. The results thus obtained are as follows:

$$(1)\ G\left(\frac{2^\circ}{4^\circ}\right) = 4.076 \qquad (2)\ G\left(\frac{2^\circ}{4^\circ}\right) = 3.915$$

From a large number of specimens collected from Naihyori veins, we could find only one having the distinct crystal faces such as a (100), c (001) and σ (103) shown in Fig. 2. The facial angles of those are as follows:

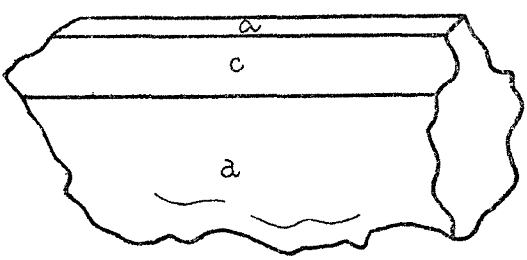

Fig. 2

		Dana
a^c (= β)	65°00′	64°59′
c^σ	22°06′	22°19′
a^σ	87°24′	87°18′

The optical properties of a thin section parallel to (001) made up from this specimen were determined by using the universal stage microscope. Biaxial negative. Optic plane is in (010). $2V = 51.4^\circ \sim 55^\circ$ $c \wedge x = 57^\circ 01'$. Pleochroism X = nearly colorless to pale brown, Y = brown, Z = pale brown, partly both Y and Z = dark brown. In several other specimens, the central part of crystal shows dark reddish brown, while the outer part, pale brown pleochroism to the direction Z. Moreover, the former shows usually greater index of refraction and smaller index of double refraction than those of the latter. These differences are generally shown in gradual change, but very rarely there exists a distinct boundary between them. We consider that the difference probably comes from the original difference of chemical compositions, and not from the weathering alteration of allanite meterial.

Chemical analysis: The chemical analysis of the foregoing two specimens shows the following results:

Component	(1)	(2)	Component	(1)	(2)
SiO_2	32.99	33.00	ThO_2	0.59	0.44
Al_2O_3	14.68	17.04	Ce_2O_3	12.06	10.61
Fe_2O_3	1.85	2.82	Ce-group Rare Earths	11.20	9.41
FeO	12.53	10.01	Y-group Rare Earths	0.47	0.91
CaO	10.03	11.62	TiO_2	1.35	0.73
MgO	0.77	0.92	$H_2O^{+)}$	0.42	0.70
			$H_2O^{-)}$	0.49	0.53
MnO	0.82	0.66	Total	100.23	99.40

According to these results, the content of each component does not show a noticeable differences between (1) and (2) except with those of Al_2O_3 and FeO, notwithstanding the difference of their paragenetic character. It is quite noticeable that the content of water is notably small in comparison with that of any other specimen hitherto found in Japan, Korea, anP South Manchuria. In the specimen of those localities, even if it seems to be in a fresh state, the content is usually 1.5% ~ 2% and sometimes 17% ~ 20%. Considering that allanite is easily decomposed by weathering, it is natural to ascribe this fact to secondary hydration. The allanite now in question, on the other hand, can be considered as quite anhydrous and fresh, almost free from the weathering alteration which Hermann has named Bucklandite. For the determination of rare earth elements, the *X*-ray spectroanalysis was undertaken by using the Siegbahn type *X*-ray spectrometer. The specimens studied in this experiment are the same as those used for the determination of the specific gravities. The determined spectre lines are as follows:

Spectre Line (in X unit)

Element	α_1	α_2	β_1	β_2	β_3	β_4	γ_1	γ_2	γ_3	γ_4
57 La	2659.7	2668.9	2453.3	2298.0	2405.3	2443.8	2137.2	——	——	——
58 Ce	2556.0	2565.1	2352.3	2204.0	2306.1	2345.2	2045.5	1956.1	1951.5	1895.
59 Pr	2459.7	2467.6	2253.9	2114.8	2212.4	——	——	——	——	——
60 Nd	2365.3	2375.6	2162.2	2031.4	2122.2	——	1873.8	——	——	——
61 Il	——	——	——	——	——	——	——	——	——	——
62 Sm	2195.0	2205.4	——	——	——	——	——	——	——	——
63 Eu	2116.3	——	——	——	——	——	——	——	——	——
64 Gd	2041.9	——	——	——	——	——	——	——	——	——

According to the observed intensity of $L\alpha_1$ spectre lines, the content of each element, in the following order, approximately agrees with Harkin's law, 58Ce, 57La, 60Nd, 59Pr, 62Sm, 64Gd, 63Eu.

Chemical composition : In order to determine the chemical composition of this mineral, the molecular ratio of each component was respectively calculated from the analytical results just mentioned above. In this calculation, we have adopted the number 144.68, especially obtained from the weight ratio of oxide to sulphate as the average atomic weight of Ce-group rare earths. Because of the small contents of the Y-group rare earths, their average atomic weight, however, was not determined and we used the mean value 156.8 of the known atomic weights of those elements. The results calculated, concerning the two specimens, are as follows :

1. Bivalent elements : $R^{II}O$ (CaO, MgO, MnO, FeO)
   (1) 0.3840 (2) 0.3786
2. Trivalent elements : $R_2^{III}O_3$ (Fe_2O_3, Al_2O_3, Ce_2O_3, Ce-group and Y-group rare earths.)
   (1) 0.2285 (2) 0.2509
3. Tetravalent elements : ThO_2
   (1) 0.0022 (2) 0.0019
4. Acidic elements : SiO_2, TiO_2
   (1) 0.5662 (2) 0.5586
5. H_2O
   (1) 0.0506 (2) 0.0683

Assuming that the component ThO_2 is contained in the form $ThSiO_4$ (Thorite), we have deducted the value of SiO_2 corresponding to that of ThO_2, from its total values. Thus, the remainder is in the following ratio :

(1) $R^{II}O : R_2^{III}O_3 : (Si, Ti)O_2 : H_2O = 0.3840 : 0.2285 : 0.5640 : 0.0506 = 4.07 : 2.42 : 6 : 0.57$

(2) $R^{II}O : R_2^{III}O_3 : (Si, Ti)O_2 : H_2O = 0.3786 : 0.2509 : 0.5567 : 0.0683 = 4.08 : 2.70 : 6 : 0.73$

Experimental formulas of the composition are expressed as follows :

(1) $4.07RO \cdot 2.42R_2O_3 \cdot 6.00(Si, Ti)O_2 \cdot 0.54H_2O$

(2) $4.08RO \cdot 2.70R_2O_3 \cdot 6.00(Si, Ti)O_2 \cdot 0.73H_2O$

In regard to the chemical composition of allanite, several discussions had been hitherto made by chemists and mineralogists, such as A. Michel-Levy, R. Hermann, N. Kockskaroff. N. Engstrom proposed the following two kinds of chemical formulas from the several analytical results : for fresh allanite as (1) and for somewhat weathered allanite as (2)

(1) $2(2RO,\ SiO_2) \cdot 3R_2O_3 \cdot 4SiO_2 \cdot H_2O$

(2) $2(2RO,\ SiO_2) \cdot 3R_2O_3 \cdot 4SiO_2 \cdot 2H_2O$

P. Groth proposed another form considering it as the basic orthosilicate. $Ca_2(AlOH)(Al, Ca, Fe)(SiO_4)_3$.

In these two formulas, the molecular ratios of respective constituents $R^{II}O$, R_2O_3, SiO_2 and H_2O are in 4 : 3 : 6 : 1 in the fresh mineral, which is somewhat apart from our results. Calculating the valency values of basic elements, we obtain the following number from our experimental formulas:

(1) $2 \times 4.07 + 3 \times 2 \times 2.42 = 22.66$

(2) $2 \times 4.08 + 3 \times 2 \times 2.70 = 24.36$

These numbers approximately agree with the valency value 24 of acidic radical SiO_4'''' as the orthosilicate mineral within the experimental error.

This fact means that there is perfect valency equilibrium between the basic elements and the acidic radicals forming an orthosilicate structure.

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