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Chemical Studies of Minerals Containing Rarer Elements from the Far East District. LXIV.[1] Abukumalite from Fusamata, Kawamata-machi, Fukushima Prefecture, Japan

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Abukumalite was first described by Hata(1938)[2] from a granite pegmatite at Suishoyama, Kawamata-machi (formerly called Iisaka Village), Fukushima Prefecture, Japan. In 1939, Machatschki[3] pointed out the isostructural relation between abukumalite and apatite due to the isomorphous coupled substitution of CaP by YSi, this being later confirmed by Omori and Hasegawa.[4] Recently, Ito(1968)[5] synthesized the intermediate members between $Ca_{10}P_6O_{24}(OH)_2$ and $Ca_6Y_4Si_6O_{24}(OH)_2$ to suggest the presence of continuous solid solution series between them, though not fully substantiated by natural materials, but partially by such a yttrian apatite as that from Naegi, Gifu Prefecture, Japan, containing 10.65% Y_2O_3 (Omori and Konno, 1962)[6] and abukumalites. Also a rare-earth ($\Sigma Ce > \Sigma Y$) silicatian apatite is reported from the Adirondack Mountains, New York.[7]

The localities of abukumalite reported thereafter include Shinden, Gifu Prefecture, Japan,[8] Hiradani, Shiga Prefecture, Japan,[9] northwestern U.S.S.R.,[10] and Pyörönmaa, Finland.[11] An aluminian variety has been reported from Siberia[12] and a cerian variety, an intermediate of abukumalite and britholite has been reported from Kola Peninsula.[13] Those from the last three foreign localities are in thermally recoverable metamict state.

The pegmatite at Fusamata, Kawamata-machi, Fukushima Prefecture, is located about 2 kilometers north of Suishoyama pegmatite, the original locality of abukumalite. In the former are known such rare earth minerals as gadolinite,[14] allanite, yttrialite, iimorite,[15] thorogummite, fergusonite, xenotime, and rare-earth-bearing zircon. The studied abukumalite was found in the dump as dark reddish brown masses up to 1 cm across and superficially coated by thorogummite.

The present report deals with the chemical analysis to specify the abukumalite from Fusamata as a fluorine dominant variety of abukumalite, and also with the determination of distribution patterns of lanthanoids in this abukumalite and that from the original locality to designate them as the members of thalenite-type (Goldschmidt and Thomassen, 1924).[16]

Chemical Composition

Chemical analysis was carried out on hand-picked material of about 3 g adopting the usual procedure for the rare earth-bearing silicates. The average atomic weight of the rare earths was determined by titrating the weighed mixed oxides with EDTA after dissolving them in hydrochloric acid. Fluorine was determined by the method proposed by Ellestad (1964).[17]

The result of chemical analysis is given in Table 1 in which that of the original abukumalite (Hata, 1938)[2] is also tabulated for comparison. The calculation of the analysis based on $O+OH+F=13$ gives $(\Sigma\, Y_{2.905}Ca_{1.388}Mn_{0.424}Fe^{3+}{}_{0.115}Fe^{2+}{}_{0.100}Al_{0.040}Na_{0.023}K_{0.015})_{5.010}(Si_{2.694}P_{0.204}Al_{0.102})_{3.000}O_{12.000}(F_{0.581}(OH)_{0.279}O_{0.140})_{1.000}$, well accounting for the ideal formula $Ca_2Y_3(SiO_4)_3(F, OH)_2$ with minor substitution of Ca by Mn, Fe, *etc.*, and the relation $F > OH$, differing from the original abukumalite in which $OH > F$.

X-Ray Studies

The precession photographs show it to be hexagonal with $a_0 = 9.44_1$ Å and $c_0 = 6.79_0$ Å, respectively, with the systematic extinction rule as: no condition for $hkil$ and $l = 2$ n for $000l$. Thus the possible space group is C_6^2, C_{6h}^2, or D_6^2. Though the preference should be due to its structural study, it is very probable that

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Table 1. Chemical analyses of abukumalites

	1	2				
	wt%	wt%	Molecular quotient	Metal number	Oxygen number	Metal number as O+OH+F=13
SiO_2	20.84	22.59	0.3760	0.3760	0.7519	2.694
P_2O_5	5.84	2.02	0.0142	0.0285	0.0712	0.204
Al_2O_3	1.05	1.01	0.0099	0.0198	0.0297	0.142
Fe_2O_3	2.10	1.28	0.0080	0.0160	0.0240	0.115
FeO		1.00	0.0139	0.0139	0.0139	0.100
MnO	1.13	4.20	0.0592	0.0592	0.0592	0.424
CaO	13.53	10.86	0.1937	0.1937	0.1937	1.388
$\sum Ce_2O_3$	6.45	56.37	0.2028	0.4055	0.6083	2.905
$\sum Y_2O_3$	45.98					
ThO_2	0.90					
Na_2O		0.11	0.0016	0.0032	0.0016	0.023
K_2O		0.10	0.0011	0.0021	0.0011	0.015
F	0.45	1.54	0.0811			0.581
$H_2O(+)$	0.58	0.35	0.0194	0.0389	0.0194	0.279
$H_2O(-)$	0.16	0.29				
CO_2	0.05					
$-O{=}F_2$	−0.19	−0.65				
Total	99.09[a]	101.07				

1. Abukumalite. Suishoyama, Kawamata-machi, Fukushima Prefecture, Japan. After Hata(1938). Mean atomic weight of rare earths=112.
   a) includes MgO 0.22.
2. Abukumalite. Fusamata, Kawamata-machi, Fukushima Prefecture, Japan. The present study. Mean atomic weight of rare earths=115.

Table 2. X-ray powder data for abukumalites and synthetic $Ca_4Y_6Si_6O_{24}(OH)_2$

1		2		3				*hkil*
d(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*Q*obs	*Q*cal	
		4.71	5					$11\bar{2}0$
4.07	20	4.07	55	4.09	20	0.060	0.060	$20\bar{2}0$
		3.88	25	3.88	15	0.066	0.067	$11\bar{2}1$
3.50	20			3.50	5	0.082	0.082	$20\bar{2}1$
3.40	40	3.411	40	3.401	10	0.0865	0.0868	0002
3.14	40	3.144	35	3.134	30	0.1019	0.1018	$10\bar{1}2$
3.08	30	3.074	40	3.089	35	0.1048	0.1047	$21\bar{3}0$
2.81	100	2.805	100	2.815	100	0.1262	0.1262	$21\bar{3}1$
2.76	60	2.769	90	2.756	65	0.1317	0.1317	$11\bar{2}2$
2.72	40	2.710	85	2.727	40	0.1345	0.1346	$30\bar{3}0$
2.62	20			2.612	10	0.1466	0.1466	$20\bar{2}2$
2.27	10	2.256	15	2.267	10	0.1945	0.1944	$31\bar{4}0$
		2.120	3	2.126	5	0.2212	0.2214	$30\bar{3}2$
2.04	10	2.046	10	2.042	10	0.2398	0.2393	$40\bar{4}0$
							0.2401	$11\bar{2}3$
1.940	30	1.932	35	1.939	15	0.2661	0.2650	$20\bar{2}3$
							0.2663	$22\bar{4}2$
1.893	10	1.883	20	1.885	10	0.2815	0.2812	$31\bar{4}2$
1.883	10	1.867	10					$32\bar{5}0$
1.829	30	1.826	35	1.826	20	0.2999	0.2999	$21\bar{3}3$
1.806	10	1.798	20	1.808	10	0.3058	0.3059	$32\bar{5}1$
1.786	20	1.776	15	1.783	10	0.3147	0.3141	$41\bar{5}0$
1.751	20	1.746	25	1.751	20	0.3262	0.3261	$40\bar{4}2$
1.705	20	1.705	15	1.696	10	0.3476	0.3470	0004
$a_0=9.43$ Å		$a_0=9.40$ Å		$a_0=9.441$ Å				
$c_0=6.81$ Å		$c_0=6.81$ Å		$c_0=6.790$ Å				

1. Abukumalite. Suishoyama, Kawamata-machi, Fukushima Prefecture, Japan. Cu/Ni radiation. Diffractometer method. After Sakurai and Kato (1962).
2. Synthetic $Ca_4Y_6Si_6O_{24}(OH)_2$. After Ito (1968).
3. Abukumalite. Fusamata, Kawamata-machi, Fukushima Prefecture, Japan. Cu/Ni radiation. Diffractometer method. The present study.

abukumalite has the same space group as ordinary apatite, C_{6h}^2.

X-ray powder data are obtained by diffractometer method employing Cu/Ni radiation. They are well coincident with those of abukumalite from the original locality, Suishoyama neighbouring to Fusamata and synthetic $Ca_{10}(PO_4)_6(OH)_2$ (Ito, 1968)[5] as shown in Table 2.

Optical Propertites

Though nearly colorless in thin section, the studied abukumalite is light brown in thick spinters with very weak dichroism: O=colorless to light brown, E=light brown; O<E.

It is uniaxial positive and the refractive indices measured by immersion method are: $\omega=1.773$, $\varepsilon=1.777$, $\varepsilon-\omega=0.004$. These values are within the variation range of those of abukumalites[8]: $\omega=1.750$—1.780, $\varepsilon=1.752$—1.783.

The Distribution Pattern of Lanthanoids

The distribution of lanthanoids in two abukumalites from Fusamata and Suishoyama was studied adopting about 0.5 g extracted rare earth oxides by x-ray fluorescent method, and Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Yb were detected. The result of the quantitative analysis of the elements including relative error of less than 10% are plotted *versus* atomic numbers (Fig. 1). The patterns obtained show a close resemblance between Fusamata and Suishoyama abukumalites, both belonging to thalenite-type as defined by Goldschmidt and Thomassen (1924).[16] The same tendency is also found in abukumalites from Shinden,[8] Hiradani,[9] and Pyörönmaa.[11]

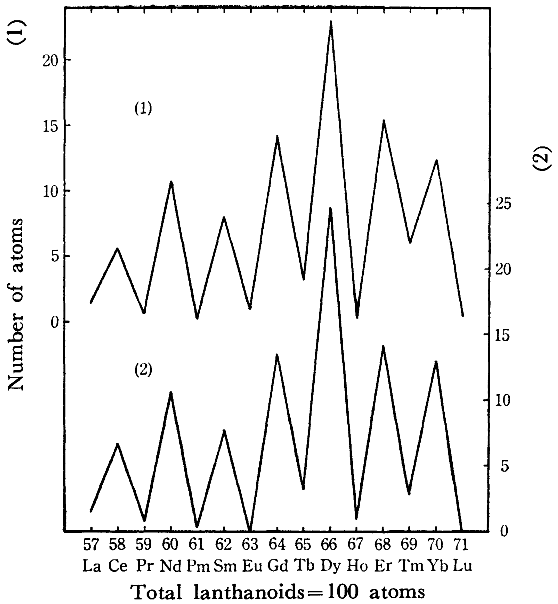

Fig. 1. Distribution patterns of lanthanoids.
(1) Abukumalite from Suishoyama, Fukushima Pref., Japan.
(2) Abukumalite from Fusamata, Fukushima Pref., Japan.

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