BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2725—2728 (1969)

Chemical Studies of Minerals Containing Rarer Elements from the Far East. LXIII. Bastnaesite from Karasugawa, Fukushima Prefecture, Japan

Kin-ichi SAKURAI,[*] Hisanobu WAKITA,[**] Akira KATO[*] and Kozo NAGASHIMA[**]

[*] *Department of Geology, National Science Museum, Ueno Park, Tokyo*

[**] *Department of Chemistry, Faculty of Science, Tokyo Kyoiku University, Otsuka, Tokyo*

(Received March 18, 1969)

The chemical analysis of bastnaesite formed as an alteration product of allanite from a granite pegmatite at Karasugawa, Nashidaira, Fukushima Prefecture, gave: Rare earths 74.4, CO_2 12.8, F 6.4, $H_2O(+)$ 2.1, $H_2O(-)$ 1.5, Rem. 3.3, $-O=F$ 2.7, total 97.8%. The distribution pattern of lanthanide elements agreed well with that of the ordinary bastnaesite. The infrared absorption spectra indicate the vicarious substitution of OH^- for F^-.

Occurrence

The Karasugawa pegmatite is situated at Nashidaira, Fukushima City, and has been worked for feldspar and quartz for several years. It is in a biotite granodiorite body and is composed mainly of microcline-perthite and quartz with large tourmaline crystals. In this pegmatite β-fergusonite,[1,2] xenotime,[3] zircon, and monazite are known to occur. The present study has added bastnaesite to this list; this is the first reported occurrence of this mineral in Japan.

The bastnaesite found in the quarry dump occurs as an alteration product of allanite in microcline-perthite crystals containing quartz and muscovite, surrounding the allanite as a white, powdery crustification or replacing it. The other associated mineral is dark brown granular xenotime, with a_0=6.91$_8$Å and c_0=6.06$_0$Å, according to the X-ray powder study. Generally the allanite crystals are long and prismatic, less than one centimeter in length and two millimeters in diameter.

Table 1. X-ray powder data for bastnaesites from Birthday Claim, California and Karasugawa, Fukushima City, Japan

1.		2.				
d(Å)	I	d(Å)	I	Q_{obs}	Q_{cal}	$hkil$
4.881	42	4.89	60	0.042	0.042	0002
3.564	71	3.550	75	0.079	0.079	$11\bar{2}0$
2.879	100	2.870	100	0.1214	0.1214	$11\bar{2}2$
2.610	1	2.602	10	0.1477	0.1479	$20\bar{2}2$
2.445	9	2.438	20	0.1683	0.1683	0004
2.273	3					$10\bar{1}4$
2.238	3					$20\bar{2}3$
2.057	42	2.050	25	0.2380	0.2380	$30\bar{3}0$
2.016	42	2.009	40	0.2477	0.2476	$11\bar{2}4$
1.898	42	1.889	25	0.2804	0.2801	$30\bar{3}2$
1.783	9	1.772	5^b	0.3186	0.3173	$22\bar{4}0$
1.674	21	1.670	15	0.3587	0.3594	$22\bar{4}2$
1.629	1					0006
1.573	15	1.571	10	0.4054	0.4063	$30\bar{3}4$
1.481	9	1.478	5	0.4581	0.4580	$11\bar{2}6$
1.439	11	1.434	10	0.4861	0.4856	$22\bar{4}4$
		1.344	5^b	0.5534	0.5553	$41\bar{5}0$
1.298	15	1.294	10	0.5969	0.5974	$41\bar{5}2$
1.277	7					$30\bar{3}6$
a_0=7.129 Å		a_0=7.10$_1$ Å				
c_0=9.774 Å		c_0=9.75$_0$ Å				

1. Bastnaesite. Birthday Claim, Mountain Pass, California. Cu/Ni radiation. After Glass *et al.* (1958).
2. Bastnaesite. Karasugawa, Nashidaira, Fukushima City, Japan. Cu/Ni radiation. The present study.

b=broad.

X-Ray Powder Diffraction and Optical Studies

The X-ray powder study was made on hand-picked material and gave the powder data shown in Table 1, in which the data for bastnaesite from Birthday Claim, Mountain Pass, California (Glass *et al.*, 1958)[4] are also tabulated for the sake of comparison. The present data are indexed with a hexagonal symmetry, with a_0=7.10$_1$Å and c_0=9.75$_0$Å; this satisfies the extinction rule required by the $P\bar{6}2c$ space group except for ($20\bar{2}2$).

Under the microscope, it is seen to be an aggregate of very fine grains. For this reason, the refractive indices measured are not always accurate. They are $n_1=1.72\pm0.01$ and $n_2=1.82\pm0.01$ respectively, both very close to the ω and ε of values bastnaesites hitherto studied.

Chemical Composition

The results of chemical analysis carried out on about 20 mg of hand-picked material are given in Table 2, together with those on F- and OH-bastnaesite obtained in Aleksandrov's study[5] and with those of the ideal bastnaesite with the formula of $CeFCO_3$. The H_2O content of Karasugawa bastnaesite is higher than that of natural F-bastnaesite, but lower than that of natural OH-bastnaesite,

Table 2. Chemical analysis

	$CeFCO_3$ %	F-Bastnaesite %	OH-Bastnaesite %	Karasugawa Bastnaesite %
RE_2O_3	74.90	64.10	75.20	74.4
CO_2	20.08	16.67	20.70	12.8
F	8.67	7.42	0.22	6.4
H_2O (+)		0.80	4.00	2.1
H_2O (−)		0.40	0.30	1.5
Rem.		14.56	0.30	3.3
	103.65	103.95	100.72	100.5
O=F	3.65	3.12	0.09	2.7
Total	100.00	100.83	100.63	97.8

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[1] K. Nagashima, A. Kato and M. Chiba, Preprints for 20th Annual Meeting of the Chemical Society of Japan (April, 1967).

[2] O. Nagashima, "Chigaku-kenkyu," **17**, Nos. 10, 11, 12, p. 42 (1966) (in Japanese).

[3] H. Wakita and K. Nagashima, *Kōbutsugaku Zasshi*, **9**, 92 (1968) (in Japanese).

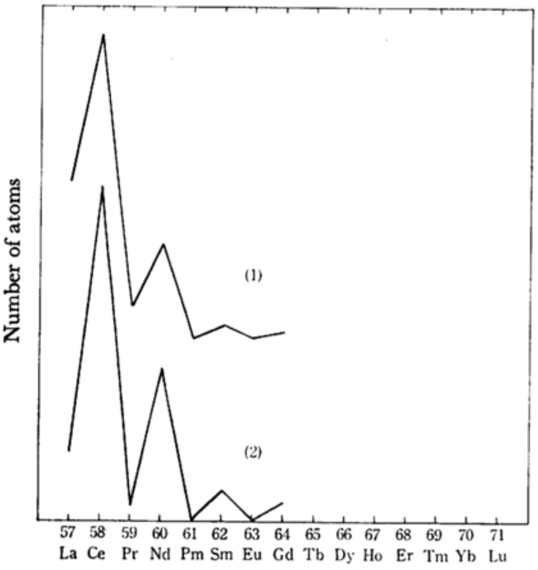
[4] J. J. Glass, H. T. Evans, Jr., M. K. Carron and F. A. Hildebrand, *Amer. Mineral.*, **43**, 460 (1958).

[5] I. V. Aleksandrov, V. I. Ivanov and L. A. Sin'kova, Zap. VMO, 3rd Ser., Part XCIV, Fasc. 3(1965) (in Russian).

suggesting partial replacement of F^- ions by OH^- ions.

The Distribution Pattern of Rare Earth Elements

The distribution of lanthanum-group elements was determined by the X-ray fluorescent method; we found lanthanum, cerium, praseodymium, samarium, and gadolinium, with the maxima at lanthanum and cerium. The quantitative estimation obtained as atomic percentages including a relative error of less than 10% is plotted the *versus* atomic numbers in Fig. 1; the figure shows a fundamental coincidence between the distribution pattern of the present bastnaesite and that called the "allanite type" by Goldschmidt and Thomassen.[6]



Total lanthanoids=100 atoms

Fig. 1. Distribution of rare earth elements.
(1) Bastnaesite from Mountain Pass, Calif., U.S.A. E.I. Semenov and R.L. Barinskii, "Geochemistry," No. 4, 398 (1958)
(2) Bastnaesite from Karasugawa (this work)

Infrared Spectroscopy

The presence of OH^- ions instead of F^- in bastnaesite is very probable, as is indicated by the X-ray diffraction study showing the isostructural relation between OH-bastnaesite and F-bastnaesite, both of which belong to the same space group, D_{3h}^4. The infrared spectrum of the natural OH-bastnaesite, composed of superposed two kinds of spectra[7], involves carbonate groups with a local symmetry of C_{3h} and with less symmetrical surroundings. The former gives rise to no band splitting, whereas the latter does as a result of the presence of OH^-.

In the infrared spectra of the present heated bastnaesite, there are absorption bands of strong or medium intensities at the following frequencies: 3630, 3470, 1450, 1020, 870, 730, and 680 cm^{-1}. Basically the spectrum is determined by the vibrations of the $(CO_3)^{2-}$ group, which has D_{3h} point symmetry and C_{3h} local symmetry in the unit cell of bastnaesite. The absorption bands at 3630, and 3470 cm^{-1} are attributable to absorption by the OH group, while that at 1020 cm^{-1} may be attributed to absorption by impurities in natural bastnaesite (SiO_2, Al_2O_3). The absorption at 1660 cm^{-1} due to molecular water is not strong. The spectrum of our sample was less split than that of M.V. Akhmanova. Chemical analysis shows that Karasugawa bastnaesite has a lower H_2O content than the OH-bastnaesite in Akhmanova's

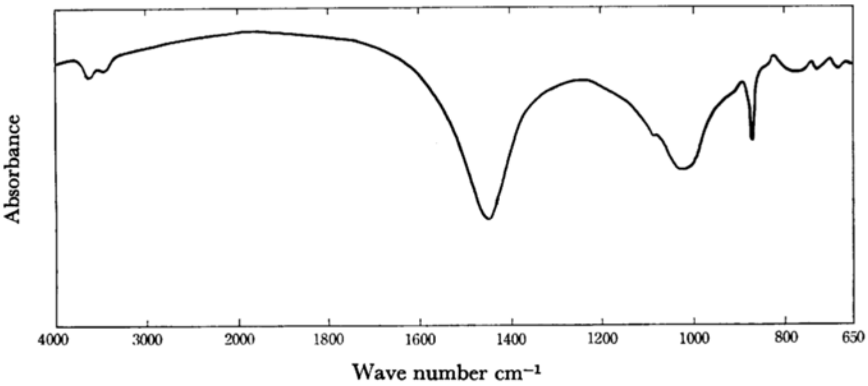


Fig.2. Infrared spectra of Karasugawa bastnaesite. KBr disk, 110°C, 48 hr, heated

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[6] V. M. Goldschmidt and L. Thomassen, Vidensk. Skrifter 1. Mat.-naturv. Klasse, **1924**, No. 5.

[7] M. V. Akhmanova and L. P. Orelova, *Geochemistry International*, **3**, 444 (1966).

study, so the infrared spectrum of Karasugawa bastnaesite may be less split than that of Akhmanova.

The authors wish to express their thanks to Mr. Otokichi Nagashima for his interest in this work, and for his help in collecting the materials. We also wish to thank Mr. Kyuzaburo Furuhashi for determining water and carbon dioxide contents for us.