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New data for iimoriite

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Abstract

Iimoriite, $Y_2(SiO_4)(CO_3)$, has been identified from Bokan Mountain on Prince of Wales Island, Alaska; it is the first reported occurrence of this mineral outside of Japan. The mineral occurs in a thorite- and uraninite-bearing quartz and albite vein.

Iimoriite occurs in subhedral to anhedral grains that range from 0.01 to 0.5 mm in diameter. The mineral is buff-tan and has a Mohs hardness of 5.5 to 6., $D_m = 4.47$, $D_c = 4.56$ (using the Gladstone–Dale relationship), and $D_c = 4.91$ (using calculated formula weight and cell volume). The luster is vitreous, and the streak is white. The mineral shows at least one good cleavage and does not fluoresce under either short-wave or long-wave ultra-violet light. It is slightly soluble in cold HCl. Optically, iimoriite is biaxial negative with refractive indices $\alpha = 1.753$, $\beta = 1.824$, $\gamma = 1.830$; $\gamma - \alpha = 0.077$; $2V_x$ (meas.) = 31°; $2V_x$ (calc.) = 31.5°. The optic plane is parallel to a cleavage direction. It is colorless and shows no pleochroism in thin section. The mineral is triclinic with space group *P*1 or $P\bar{1}$, and least-squares refinement of 60 reflections from X-ray powder data yields: $a = 6.573(1)$, $b = 6.651(1)$, $c = 6.454(1)$Å, $\alpha = 116.44°$, $\beta = 92.34°$, $\gamma = 95.63°$, $V = 250.30(6)$Å^3. Z = 2. The eight strongest lines in the X-ray powder pattern are (*d* in Å, intensity, *hkl*) 2.88(100) (002 and $\bar{1}11$), 2.95(80)($\bar{2}01$), 2.78(40)($0\bar{2}2$), 3.02(36)($\bar{2}10$), 2.84(35)($\bar{1}\bar{2}1$), 2.70(29)(210), 3.30(27)($0\bar{2}1$), and 4.54(25)($\bar{1}01$).

Iimoriite was analyzed by a combination of several analytical methods. A calculated structural formula for the Bokan Mountain iimoriite (on the basis of 7 oxygens) is: $(Y_{1.44}La_{0.002}Ce_{0.008}Pr_{0.002}Nd_{0.004}Sm_{0.008}Gd_{0.04}Eu_{0.002}Tb_{0.02}Dy_{0.11}Ho_{0.03}Er_{0.11}Tm_{0.01}Yb_{0.08}Lu_{0.09}Fe^{+3}_{0.02}Ca_{0.01})_{1.95}Si_{1.12}O_4[(CO_3)_{0.91}(H_2O^+)_{0.14}]_{1.05}$.

Introduction

Iimoriite, $Y_2(SiO_4)(CO_3)$ (as described herein), was first described by Kato and Nagashima (1970) as $Y_5(Sio_4)_3(OH)_3$ that came from pegmatites at Fusamata and Suishoyama, Kawatamachi, Fukushima Prefecture, Japan. More recently it has been found at Bokan Mountain, Prince of Wales Island, Alaska. The first samples from Alaska were collected in 1975. Mineralogical studies have now been completed on the Alaskan material along with partial data for type material to permit some corrections and additions to the data originally published by Kato and Nagashima (1970). Because of significant differences in its chemistry and unit-cell data *vs.* those reported for iimoriite from Japan, the Alaskan iimoriite was at first thought to be a new mineral. Study of type iimoriite (120635), provided by John Sampson White, Jr. (U.S. National Museum of Natural History) at the suggestion of A. Kato, indicated that the two were the same species. Dr. Kato also kindly provided unpublished data and information on the Japanese material from his files.

Occurrence

Iimoriite occurs within a vein on the I and L no. 4 claim on the southeast side of Bokan Mountain, which is near the east side of the southern part of Prince of Wales Island. Bokan Mountain is approximately 64 km southwest of Ketchikan in the southern part of the Alaskan panhandle. The I and L no. 4 claim was originally located for its uranium content in 1955 by L. A. and Irma Hollenbeak (MacKevett, 1963). Iimoriite occurs only in the northernmost of nine veins that form the northwest end of the I and L vein system (Staatz, 1978). All nine veins are emplaced into Bokan Mountain granite of Triassic or Lower Jurassic age (Lanphere *et al.*, 1964). This rock is an uncommon type, being a peralkaline riebeckite- and acmite-bearing granite (MacKevett, 1963). The iimoriite-bearing vein has been traced for 277 m and varies in width from 2.5 mm to 1.5 m (Staatz, 1978). A total of 24 minerals have been identified in this vein, but some are quite rare and have only been found locally. Quartz and albite are the principal gangue miner-

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als. Iimoriite has been found in only two places in this vein, where it is associated with siderite. Other rare-earth minerals include bastnaesite and xenotime, but neither was found in the same samples as the iimoriite. Thorite and uraninite are the principal radioactive minerals. Other minerals commonly found in small amounts include fluorite, zircon, pyrite, magnetite, sphalerite, and galena. A complete list of all of the minerals occurring in various samples has been previously published (Staatz, 1978).

The rare-earth content (atomic nos. 57–71, plus 39) of six samples varied from 0.70 to more than 5.5 percent total rare earths. This vein is unusual because in parts of it cerium-group rare earth elements (light rare earths, La to Gd) are more abundant than the yttrium-group rare earths (heavy rare earths, Tb to Lu, and Y), and in other parts the reverse is true. Yttrium-group rare earths predominate in the two Alaskan samples from which iimoriite was recovered, and yttrium makes up at least 2 percent of each bulk sample.

Physical properties

Iimoriite occurs as anhedral to subhedral grains as much as 0.5 mm in maximum dimension, and is medium buff-tan in color. The luster is somewhat vitreous to resinous; hardness is 5.5 to 6 (Mohs); and the streak is white. The mineral shows a slight reaction with cold HCl producing small bubbles of CO_2. It shows at least one good cleavage, direction unknown, and it does not fluoresce under ultraviolet light. Measured density (D_m) obtained on slightly impure material using a micropycnometer is 4.47; calculated density (D_c) using the relationship of Gladstone and Dale (Mandarino, 1976, 1979) is 4.56; and D_c using formula weight and cell volume is 4.91. The calculated density for pure $Y_2(SiO_4)(CO_3)$ using our measured cell volume is 4.36.

Iimoriite is biaxial negative, $2V_x$ (measured) = 31° using a spindle stage and Na light $2V_x$ (calculated) = 31.5°. The indices of refraction are $\alpha = 1.753 \pm 0.0.002$, $\beta = 1.824 \pm 0.003$, $\gamma = 1.830 \pm 0.002$, $\gamma - \alpha = 0.077$. The mineral is colorless in thin section and shows no pleochroism. The optical axial plane is parallel to an undetermined cleavage direction.

Crystallography and X-ray diffraction data

Precession photographs (0 to 3rd level) of *h0l* and *0kl* nets using Mo*Kα* radiation (Zr-filtered) showed triclinic symmetry with possible space groups $P1$ or $P\bar{1}$. Cone-axis photographs (Mo*Kα* radiation with Zr filter) showed no evidence of the superstructure suggested by Kato and Nagashima (1970).

Measured unit cell data from the precession photographs were refined using the least-squares program of Appleman and Evans (1973) for 60 reflections (Table 1). LiF was used as an internal standard, at a scan speed of 1/8° per minute, scanned from 5° to 75° 2*θ*, using Cu*Kα* (Ni-filtered) radiation. JCPDS card no. 29-1388 should be replaced by these data because the reduced cell was not chosen, resulting in erroneous *hkl* values. Refined unit cell data, using $c < a < b$, are: $a = 6.573(1)$, $b = 6.651(1)$, $c = 6.454(1)$Å, $\alpha = 116.44°$, $\beta = 92.34°$, $\gamma = 95.63°$, $V = 250.30(6)$Å^3, Z = 2. A complete crystal structure determination has been carried out by Campana *et al.* (in prep.). Gandolfi (114 mm) photographs, made using Cu*Kα* radiation (Ni-filtered) of Bokan Mountain iimoriite and type iimoriite (Fusamata) provided by J. S. White (NMNH no. 120635), are nearly identical.

Table 1. X-ray powder diffraction data for iimoriite from Bokan Mountain, Alaska

hkl*	d_{calc} (Å)*	d_{obs} (Å)**	I_{obs}	hkl*	d_{calc}(Å)*	d_{obs}(Å)**	I_{obs}
100	6.51	6.53	13	$3\bar{2}1$	1.895	1.894	4
$\bar{1}10$	4.69	4.69	10	$\bar{1}03$	1.889	1.888	5
$\bar{1}01$	4.53	4.54	25	130	1.820	1.820	7
$1\bar{1}1$	4.30	4.29	22	103	1.794	1.794	6
$\bar{1}\bar{1}1$	4.17	4.17	17	$\bar{1}\bar{3}3$	1.770	1.770	7
101	4.12	4.12	18	$2\bar{2}3$	1.755	1.755	4
$0\bar{2}1$	3.30	3.30	27	$2\bar{1}3$	1.735	1.735	20
200	3.26	3.26	3	$\bar{1}22$	1.710	1.710	14
$\bar{2}10$	3.022	3.023	36	302	1.659	1.659	4
$\bar{2}01$	2.956	2.954	80	$\bar{3}12$	1.657	1.657	4
111,002	2.876	2.881	100	320	1.650	1.650	6
$\bar{1}\bar{2}1$	2.842	2.841	35	$3\bar{3}1$	1.633	1.632	12
$\bar{1}20$	2.831	2.827	14	$0\bar{4}1$	1.616	1.617	10
$0\bar{2}2$	2.783	2.784	40	$1\bar{4}1$	1.613	1.613	11
210	2.707	2.705	29	230	1.595	1.596	11
$\bar{2}\bar{1}2$	2.332	2.330	20	$4\bar{1}1$	1.576	1.577	3
212	2.251	2.249	20	$0\bar{4}3$	1.559	1.560	15
$\bar{2}\bar{2}1$	2.220	2.223	6	$\bar{1}\bar{4}1$	1.528	1.528	4
$0\bar{3}1$	2.190	2.189	7	$4\bar{2}1$	1.516	1.515	4
300	2.171	2.171	11	$3\bar{2}3$	1.500	1.500	4
$\bar{3}10$	2.129	2.128	11	$\bar{1}40$	1.482	1.480	3
$0\bar{2}3$	2.099	2.099	11	321	1.465	1.465	2
$1\bar{3}2$	2.072	2.071	10	$2\bar{4}3$	1.440	1.441	4
202	2.061	2.062	14	$\bar{3}22$,004	1.438	1.438	3
220	2.058	2.058	11	$\bar{2}\bar{4}2$	1.421	1.421	17
121	2.040	2.038	7	$\bar{4}21$	1.413	1.413	4
$\bar{1}\bar{3}1$	2.011	2.010	15	$\bar{4}\bar{2}1$	1.410	1.410	3
$1\bar{2}3$	1.991	1.990	11	$\bar{3}\bar{3}3$,213	1.389	1.389	2
$\bar{1}30$	1.956	1.956	16	$3\bar{4}2$	1.376	1.375	2
$2\bar{3}1$	1.916	1.916	11				

* Indices and d_{calc} were obtained using the computer program of Appleman and Evans (1973).

** X-ray diffractometer conditions were: Cu/Ni radiation, CuK_α = 1.54178Å; LiF used as an internal standard; scanned at 1/8° 2Θ per minute from 5 - 75° 2Θ.

Chemical composition

Several grams of iimoriite were separated and concentrated by heavy liquid and magnetic separation methods. The iimoriite concentrate from the Frantz isodynamic separator was then carefully hand picked. Other minerals present in the same magnetic fraction were: rutile, pyrite, fluorite, and zircon. Grains of iimoriite with visible contaminating minerals were removed. Approximately 1 gram of purified material was prepared for chemical analysis. Six-step semiquantitative emission spectrographic analysis of 10 mg yielded (in weight percents, exclusive of the REE and Si): Fe, 0.3; Mg, <0.005 percent; Ca, 1.5; Ti, 0.03; Al, <0.002; Na, <0.1; K, <0.1; P, <0.2; Li, <0.1; Mn, 0.015; Be, 0.0005; Zr, 0.3. Other elements sought and found to be below levels of detection were: Ag, As, Au, B, Ba, Bi, Cd, Co, Cr, Cu, Mo, Ni, Pb, Pd, Pt, Sb, Sc, Sn, Sr, Te, U, V, W, Zn, Ga, Ge, Hf, In, Re, Ta, Th, and Tl (Nancy M. Conklin, analyst). The spectrographic analysis shows the presence of minor

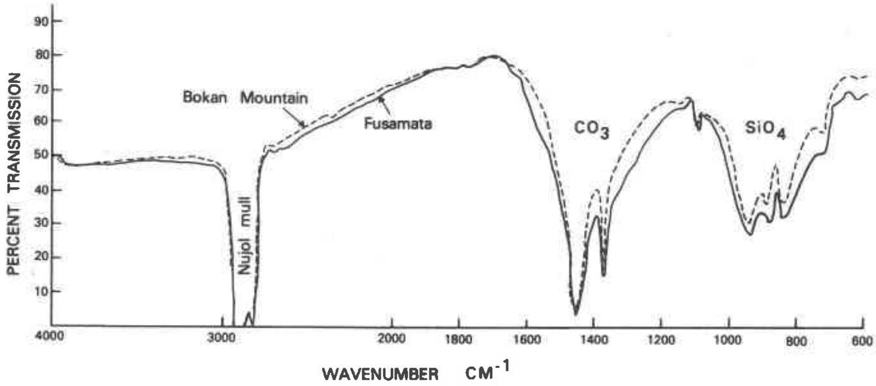

Fig. 1. Infrared transmission spectra for iimoriite from Bokan Mountain, Alaska and Fusamata, Japan.

amounts of Zr and F, suggesting the presence of inclusions of zircon and fluorite.

Chemical analysis of the Fusamata iimoriite (Kato and Nagashima, 1970) showed more P_2O_5 (0.91 weight percent), U_3O_8 (0.88), CaO (0.85), Zr,Hf)O_2 (1.43), MgO (0.71), Fe_2O_3 (1.33), Al_2O_3 (1.31), H_2O^+ (5.85) and H_2O^- (0.87) than determined for Bokan Mountain iimoriite. Values for ΣY_2O_3, SiO_2, Ce_2O_3, and ThO_2 are very similar to those obtained for iimoriite from Bokan Mountain. The values for H_2O^+ and H_2O^- for the Fusamata material as reported by Kato and Nagashima (1970) were subsequently shown to be in error (Kato, pers. comm., 1980), and the presence of major amounts of CO_3 was confirmed. Infrared spectral measurements showed the absence of detectable amounts of hydroxyl (OH), and the presence of major CO_3 and SiO_4 for both Bokan Mountain and Fusamata Iimoriite (Fig. 1).

Total water was determined with a microcoulometric moisture analyzer on approximately 50 mg of sample and H_2O^- was determined gravimetrically by heating approximately 100 mg of sample at 105±5°C for 48 hours (analyst, Marcelyn Cremer, U.S. Geological Survey, Menlo Park, Calif.).

Carbon was determined by Van E. Shaw using combustion thermal conductivity and is reported as the weighted average of two determinations of 0.11 grams and 0.247 grams respectively. Silica was determined by plasma diffusion analysis by Leon A. Bradley on 100 mg of sample. The REE were determined by N. M. Conklin by quantitative emission spectrographic analysis on 100 mg of sample, and the remaining elements (Ca,Fe,Na,K,Mg) were determined by E. E. Foord using an ARL SEM EMX electron microprobe. The electron microprobe studies showed iimoriite to be moderately inhomogeneous with respect to intragrain and intergrain REE distribution. The yttrium content varied antipathetically with the other REE. Table 2 shows the composite chemical analysis.

A calculated structural formula for the Bokan Mountain iimoriite (on the basis of 7 oxygens) is: $(Y_{1.44}La_{0.002}Ce_{0.008}Pr_{0.002}Nd_{0.004}Sm_{0.008}Gd_{0.04}Eu_{0.002}Tb_{0.02}Dy_{0.11}Ho_{0.03}Er_{0.11}Tm_{0.01}Yb_{0.08}Lu_{0.09}Fe^{+3}_{0.02}Ca_{0.01})_{1.95}Si_{1.12}O_4[(CO_3)_{0.91}(H_2O^+)_{0.14}]_{1.05}$. The simplified ideal formula is thus $Y_2(SiO_4)(CO_3)$. The crystal structure analysis by Campana *et al.* (in prep.) confirms the structural formula.

Discussion

Iimoriite at Fusamata and Suishoyama is found in granitic pegmatites. At the former locality it is associated with quartz, microcline, biotite, monazite, fergusonite, uraninite, and an unidentified mineral; at the latter locality it occurs as an alteration product of thalenite (Kato and Nagashima, 1970). The mineral at Bokan Mountain occurs in a vein, where it is associated with quartz, albite, siderite, pyrite, fluorite, sphalerite, galena, and zircon.

Calculation of chondrite normalized ratios (CNR) for the Bokan Mountain iimoriite using a computer program that treats all 15 rare earths (written by Sam Rosenblum, USGS) yields a plot very similar to those for other known silico-carbonates such as caysichite and kainosite (Fig. 2).

Table 2. Composite chemical analysis of iimoriite

Oxide	Weight percent	Oxide	Weight percent
SiO_2	19.0*	Tm_2O_3	0.6+
CO_2	11.3**	Yb_2O_3	4.4+
Y_2O_3	45.7+	Lu_2O_3	0.5+
La_2O_3	0.1+	Fe_2O_3	0.4++
Ce_2O_3	0.4+	Na_2O	0.0++
Pr_2O_3	0.1+	K_2O	0.0++
Nd_2O_3	0.2+	MgO	0.0++
Sm_2O_3	0.4+	CaO	0.1++
Gd_2O_3	2.2+	TiO_2	0.05+
Eu_2O_3	0.1+	MnO	0.01+
Tb_2O_3	0.8+	P_2O_5	<0.2+
Dy_2O_3	5.7+	H_2O^+	0.39
Ho_2O_3	1.6+	H_2O^-	0.10
Er_2O_3	5.7+	Total	99.85

* Determined by plasma diffusion by Leon A. Bradley. ** Determined by combustion thermal conductivity by Van E. Shaw. + Determined by quantitative emission spectrography by Nancy M. Conklin. ++ Determined by electron microprobe by Eugene E. Foord. H_2O (total) determined by microcoulometric moisture analysis by Marcelyn J. Cremer. H_2O^- determined gravimetrically by Marcelyn J. Cremer.
ΣREE_2O_3 = 68.5 weight percent; $\Sigma Y_{group}/\Sigma REE_2O_3$ = 98.5 percent.

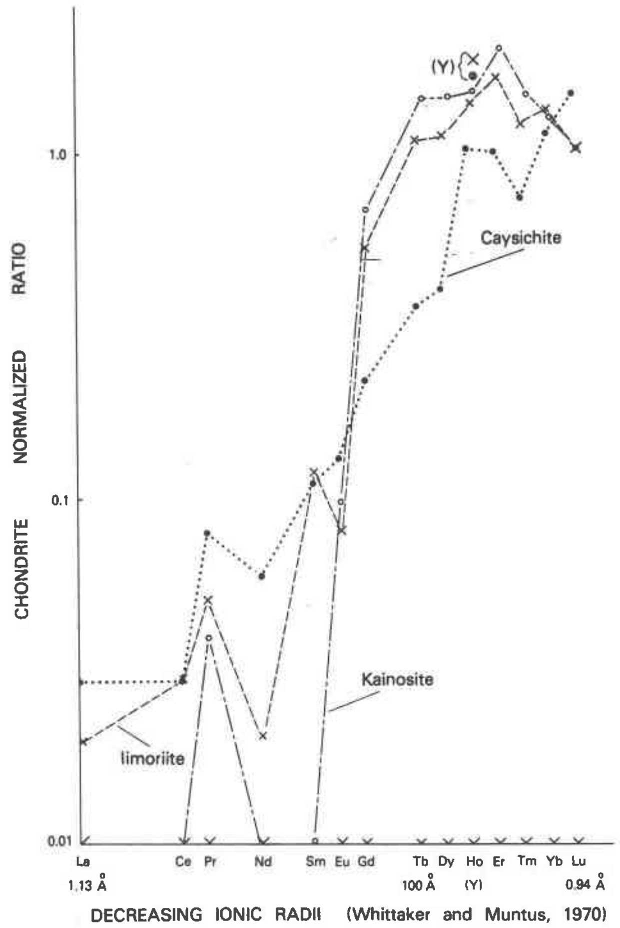

Fig. 2. Chondrite normalized ratios for iimoriite, caysichite, and kainosite.

Caysichite, a hydrated silico-carbonate of Y and Ca (Hogarth *et al.*, 1974) is generally similar to iimoriite as far as occurrence and basic chemistry are concerned. Kainosite, also a hydrated Ca–Y carbonate-silicate, has been reported to occur in granitic pegmatites (Vlasov, 1966) and thorium veins (Adams *et al.*, 1964).

Iimoriite may be more common than reported. Other rare-earth and uranium-bearing pegmatites and veins should be examined for the occurrence of this mineral.

Acknowledgments

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