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THE ATOMIC ARRANGEMENT OF IIMORIITE-(Y), $Y_2(SiO_4)(CO_3)$

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ABSTRACT

Iimoriite-(Y) from Bokan Mountain, Prince of Wales Island, Alaska has been studied using single-crystal X-ray-diffraction techniques. The mineral, ideally $Y_2(SiO_4)(CO_3)$, crystallizes in space group $P\bar{1}$, with *a* 6.5495(13), *b* 6.6291(14), *c* 6.4395(11)Å, α 116.364(15), β 92.556(15) and γ 95.506(17)°. The atomic arrangement has been solved and refined to an *R* value of 0.019. The arrangement of atoms consists of alternating $(01\bar{1})$ slabs of orthosilicate groups and carbonate groups, with no sharing of oxygen atoms between anionic complexes in adjacent slabs. Y1 atoms separate adjacent tetrahedra along [100] within the orthosilicate slab, and Y2 atoms separate adjacent carbonate groups along [100] within the carbonate slab. Adjacent orthosilicate and carbonate slabs are linked in (100) by bonding Y atoms from each slab to oxygen atoms of adjacent slabs, in the form of YO_8 polyhedra. The Y1 atoms exist in $Y1_2O_{14}$ dimers in the orthosilicate slab, and the Y2 atoms exist in continuous [011] ribbons of edge-sharing $Y2O_8$ polyhedra in the carbonate slab.

Keywords: iimoriite-(Y), crystal structure.

SOMMAIRE

Nous avons caractérisé l'iimoriïte-(Y), $Y_2(SiO_4)(CO_3)$, provenant du mont Bokan, sur l'île du Prince de Galles, en Alaska, par diffraction X sur cristal unique. Il s'agit d'un minéral triclinique, groupe spatial $P\bar{1}$, dont les paramètres réticulaires sont *a* 6.5495(13), *b* 6.6291(14), *c* 6.4395(11)Å, α 116.364(15), β 92.556(15) et γ 95.506(17)°. Nous avons affiné la position des atomes dans cette structure jusqu'à un résidu *R* de 0.019. L'iimoriïte contient une alternance de panneaux $(01\bar{1})$ de groupes orthosilicatés et de groupes carbonatés, sans partage d'atomes d'oxygène entre les complexes anioniques des panneaux adjacents. Les atomes Y1 séparent les tétraèdres adjacents le long de [100] dans le panneau orthosilicaté, et les atomes Y2 séparent les groupes carbonatés adjacents le long de [100] dans le panneau carbonaté. Les panneaux adjacents de groupes orthosilicatés et de groupes carbonatés sont rattachés dans le plan (100) par liaisons impliquant les atomes Y de chaque panneau aux atomes d'oxygène des panneaux adjacents, pour en former des polyèdres YO_8. Les atomes Y1 sont agencés en dimères $Y1_2O_{14}$ dans le panneau orthosilicaté, et les atomes Y2 forment des rubans continus d'octaèdres à arêtes partagées le long de [011] dans le panneau carbonaté.

(Traduit par la Rédaction)

Mots-clés: iimoriïte-(Y), structure cristalline.

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INTRODUCTION

Iimoriite-(Y) has been found in granitic pegmatites at Fusamata and Suishoyama, Kawatamachi, Fukushima Prefecture, Japan, and at Bokan Mountain on Prince of Wales Island, Alaska. Foord *et al.* (1984) summarized the available data on the mineral and provided a revised chemical formula derived from the results of chemical analyses and a provisional determination of the structure. On the basis of the analyses, they suggested the ideal formula $Y_2(SiO_4)(CO_3)$, with extensive substitutions of rare-earth elements for Y. They also noted that iimoriite-(Y) crystallizes in space group $P1$ or $P\bar{1}$. Because of minor problems with the structural results (R.C. Ewing, pers. comm., 1994), however, details of the atomic arrangement of iimoriite-(Y) have not been published. This study presents the structure of iimoriite-(Y), solved independently from newly acquired data.

EXPERIMENTAL

A single crystal of iimoriite-(Y) from Bokan Mountain, Prince of Wales Island, Alaska (Foord *et al.* 1984) was selected for X-ray examination; precession photographs showed sharp diffraction-spots. The crystal was oriented on a CAD4 single-crystal diffractometer, and cell parameters were obtained by least-squares refinement of the setting angles of 25 independent diffraction-maxima, utilizing graphite-monochromatized Mo*K*α radiation. Intensity data were collected on the same instrument; absorption effects were corrected by the ψ-scan method and, subsequent to structure solution, by the absorption-surface method, as implemented in program DIFABS (Walker & Stuart 1983). Methods of data collection and the results of the crystal-structure refinement are given in Table 1.

TABLE 1. CRYSTAL DATA AND RESULTS OF STRUCTURE REFINEMENTS FOR IIMORIITE-(Y)

Dimension	0.16 x 0.08 x 0.08 mm		
Unit cell (space group $P\bar{1}$)			
a(Å)	6.5495(13)	α(°)	116.364(15)
b	6.6291(14)	β	92.556(15)
c	6.4395(11)	γ	95.506(17)
Formula (ideal):	$Y_2(SiO_4)(CO_3)$		
$D_{meas.}$	4.92 g/cm^3	Formula wt.	367.87 g
θ limits	0.0 - 30°	Scan type	θ/2θ
Standards:		Scan time(s)	≤60 s
Intensity,	3 per 4 hrs	R_{merge}	0.013
Orientation,	3 per 300 reflections	R	0.019
Data collected	2897 ($\pm h$, $\pm k$, $\pm l$)	R_w	0.024
Unique data	1449	Goodness-of-fit	1.366
Data > $3\sigma_I$	1083	Variables	103
Largest peaks on difference map (e/Å^3)			
(+)*	0.69		
(-)	0.72		

Note: Numbers in parentheses denote 1 esd of last unit cited.

TABLE 2. POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR ATOMS IN IIMORIITE-(Y)

Atom	*x*	*y*	*z*	*B*(Å^2)
Y1	0.16782(6)	0.18941(6)	0.25715(6)	0.489(7)
Y2	0.41401(6)	0.70249(6)	0.25067(6)	0.347(7)
Si	0.6578(2)	0.2411(2)	0.2632(2)	0.66(3)
C	-0.0892(8)	0.7350(7)	0.1936(8)	0.78(9)
O1	0.0961(5)	0.8366(5)	0.2649(6)	0.89(7)
O2	0.5331(5)	0.3401(5)	0.1137(5)	0.79(7)
O3	0.4834(5)	0.0883(5)	0.3312(5)	0.72(7)
O4	0.1682(5)	0.9086(5)	0.8742(6)	0.83(7)
O5	0.2165(5)	0.2502(6)	0.6563(6)	0.98(7)
O6	0.1466(5)	0.3778(5)	0.0242(5)	0.87(7)
O7	0.2510(5)	0.5633(5)	0.4804(6)	0.92(7)

Anisotropically refined atoms are given in the form of their isotropic equivalent displacement parameter defined as: $(4/3) * [a^2*\beta_{(1,1)} + b^2*\beta_{(2,2)} + c^2*\beta_{(3,3)} + ab(\cos\gamma)*\beta_{(1,2)} + ac(\cos\beta)*\beta_{(1,3)} + bc(\cos\alpha)*\beta_{(2,3)}]$.

The phase problem was solved in space group $P\bar{1}$ using Patterson methods as implemented in SHELXS–86 (Sheldrick 1985). The Patterson map allowed location of both Y atoms, and successive full-matrix least-squares refinement, coupled with difference-Fourier syntheses, revealed the entire arrangement of atoms. Subsequent to the application of Patterson methods, all crystal-structure calculations were undertaken using the ENRAF–NONIUS SDP package of computer programs (Frenz 1985). Neutral-atom scattering factors, with corrections for anomalous dispersion, were employed throughout the refinement.

Chemical data for the Alaskan material were provided by Foord *et al.* (1984). The structural formula offered there is: $(Y_{1.44}La_{0.002}Ce_{0.008}Pr_{0.002}Nd_{0.004}Sm_{0.008}Gd_{0.04}Eu_{0.002}Tb_{0.02}Dy_{0.11}Ho_{0.03}Er_{0.11}Tm_{0.01}Yb_{0.08}Lu_{0.09}Fe^{3+}_{0.02}Ca_{0.01})_{\Sigma 1.95}Si_{1.12}O_4[(CO_3)_{0.91}(H_2O^{+}_{0.14}]_{\Sigma 1.05}$. To model the occupancy of the two yttrium sites, scattering factors for yttrium were employed, and multiplicity was released during refinement. The Y1 site yielded a total of 1.175(1) Y atoms, and the Y2 site yielded 1.155(1) Y atoms. The total (2.33 Y atoms) is in good agreement with the results of the chemical analysis, which yields total electron-occupancy for the two sites consistent with 2.35 Y atoms.

Bond-valence sums were calculated for all atoms in iimoriite-(Y), and are in good agreement with the formal valence of the ions. The valence sums of oxygen atoms are between 2.01 and 2.14 *vu* (valence units), and among the cations, the sums for Y1, Y2, Si, and C are 3.21, 3.08, 4.04, and 4.01 *vu*, respectively.

Table 2 contains positional parameters and equivalent isotropic-displacement parameters for atoms in iimoriite-(Y), and Table 3 contains anisotropic thermal parameters. Table 4 provides selected interatomic distances, and Table 5 gives observed and calculated structure-factors. Tables 3 and 5 have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 4. SELECTED BOND DISTANCES IN IIMORIITE-(Y)

Y1-	O1	2.364(4)Å	Y2-	O1	2.332(4)Å
	O2	2.852(4)		O2	2.388(3)
	O3	2.327(4)		O2	2.282(4)
	O4	2.339(3)		O3	2.366(3)
	O4	2.248(3)		O3	2.443(3)
	O5	2.420(4)		O5	2.423(4)
	O6	2.347(4)		O6	2.467(3)
	O7	2.240(3)		O7	2.312(4)
Mean		2.392Å	Mean		2.377Å
Si-	O2	1.618(4)	C-	O1	1.287(6)
	O3	1.655(4)		O5	1.282(6)
	O4	1.611(4)		O6	1.279(5)
	O7	1.620(3)	Mean		1.283Å
Mean		1.626Å			

Note: Numbers in parentheses denote 1 esd of last unit cited.

DISCUSSION OF THE ATOMIC ARRANGEMENT

All atoms of oxygen in iimoriite-(Y) are bonded in anionic complexes, either $[CO_3]^{2-}$ trigonal-planar carbonate groups (O1, O5, O6) or $[SiO_4]^{4-}$ tetrahedra (O2, O3, O4, O7). Because of the high Pauling bond-strength of bonds *within* the anionic complexes (1.33 *vu* in the carbonate groups, and 1.0 *vu* in the silicate tetrahedra), bonding *between* the two anionic complexes by sharing oxygen atoms is prohibited, as such a scenario would result in a carbonate–silicate "bridging oxygen" atom being overbonded by 0.33 *vu*. In addition, because there is no polymerization between silicate tetrahedra in iimoriite-(Y), all anionic complexes in the mineral are isolated and bound only to yttrium atoms. The arrangement of anionic complexes consists of alternating $(01\bar{1})$ slabs of orthosilicate tetrahedra and isolated $[CO_3]^{2-}$ carbonate groups (Fig. 1).

Within each $(01\bar{1})$ slab of anionic complexes, adjacent complexes along [100] are separated by Y atoms, Y1 atoms in the orthosilicate slab and Y2 atoms in the carbonate slab (Fig. 1). In addition to linking adjacent anionic complexes along *a*, Y atoms also link adjacent slabs of anionic complexes in (100). Both Y atoms exist in YO_8 polyhedra. The Y1 polyhedra exist as $Y1_2O_{14}$ dimers of inversion-related polyhedra, sharing an O4–O4 edge. The Y2 atoms are polymerized in continuous [011] ribbons within the carbonate slab, sharing O2–O2 and O3–O3 edges within the ribbons (Fig. 2).

An examination of the nine known mineral structures that contain carbonate groups and silicate tetrahedra revealed that none contains linkages between the carbonate groups and silicate tetrahedra in the structures, consistent with observations made in iimoriite-(Y). The rigid nature of the two polyhedra prohibits lengthening of cation–oxygen bonds to alleviate the 0.33 *vu* overbonding, preventing the polyhedral linkage.

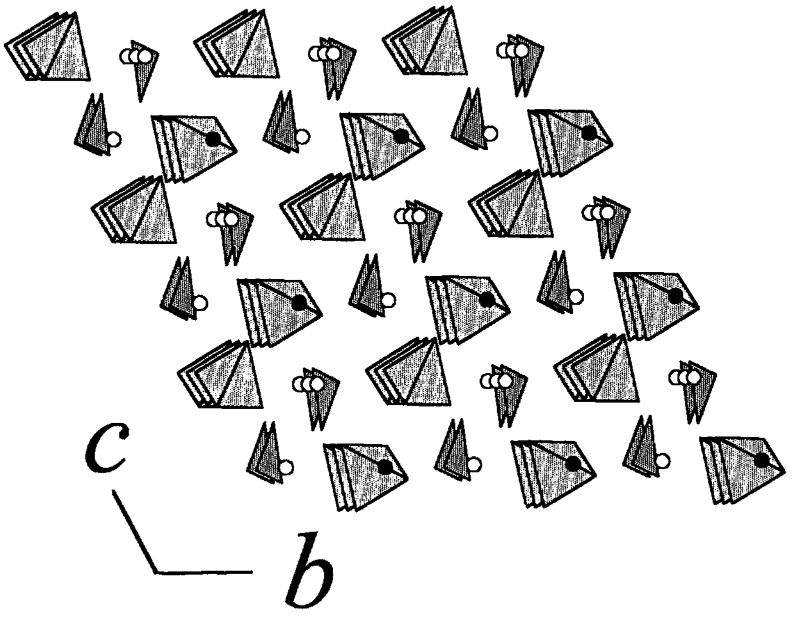

FIG. 1. Atomic arrangement of iimoriite-(Y) projected down *a**, illustrating $(01\bar{1})$ planes of orthosilicate (tetrahedra) and carbonate (triangles). The ligation of Y atoms is not illustrated. Y1 atoms (filled circles) separate tetrahedra in the orthosilicate layer, and Y2 atoms (open circles) separate carbonate groups in the carbonate layer.

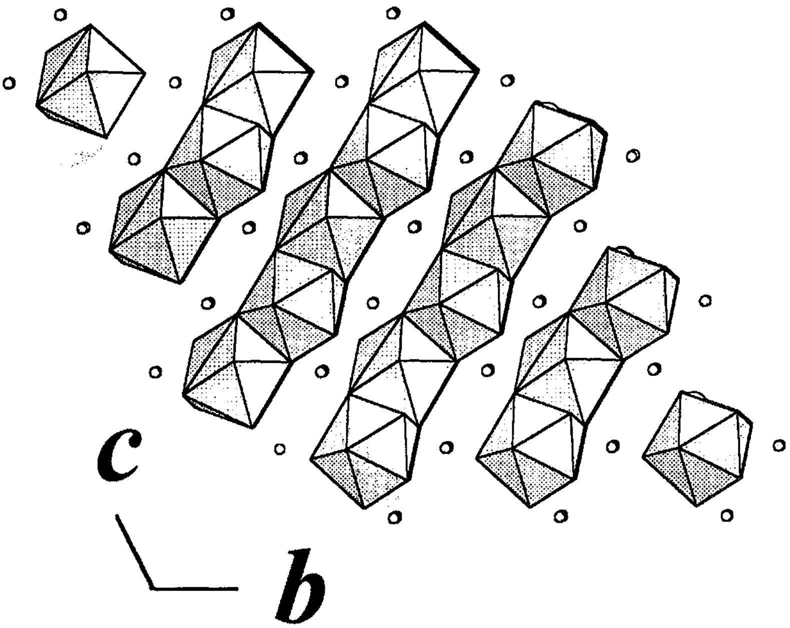

FIG. 2. Ribbons of $Y2O_8$ polyhedra in the carbonate layer of the iimoriite-(Y) structure. Small atoms are silicon atoms in the orthosilicate layer.

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