

The chemistry and crystal structure of okanoganite-(Y) and comparison with vicanite-(Ce)

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ABSTRACT

The structure of okanoganite-(Y), a rare REE-rich borofluorosilicate, was refined in space group $R3m$, starting from the atomic coordinates of vicanite-(Ce), to a final R -factor of 0.032 for 1857 observed reflections. Okanoganite-(Y) is trigonal with $a = 10.7108(5)$, $c = 27.0398(11)$ Å, $Z = 3$. SIMS procedures were used for the analysis of H, F, Li, Be, B, REE, Y, actinides (U, Th, Pb), and other trace elements (Sr, Ba, Cs). An excellent agreement was obtained by comparing EMPA + SIMS with SREF data. On the basis of 38 O atoms, the resulting unit formula is $(Y_{4.52}REE_{6.82}Ca_{2.65}Na_{1.63}Th_{0.19}Sr_{0.02}Ba_{0.01}U_{0.01})_{\Sigma 15.85}(Fe_{0.74}^{3+}Ti_{0.19}Li_{0.04})_{\Sigma 0.97}(Si_{6.71}P_{0.32}B_{2.94}Be_{0.01})_{\Sigma 9.98}(O_{34.02}OH_{3.98})_{\Sigma 38}F_{10.04}$. The chemical data are compared to those in the literature and discrepancies are discussed.

The structure of okanoganite-(Y) resembles that of vicanite-(Ce). They are the only two borosilicates showing a structural unit of threefold rings of BO_4 tetrahedra. The main differences between the two minerals lie in the different chemical composition [absence of As and low amount of Ca and Th in okanoganite-(Y); absence of Y and low amount of Na in vicanite-(Ce)] and in the lack, in okanoganite-(Y), of a B atom that is at the center of a triangular BO_3 coordination in vicanite-(Ce). Additional analogies and differences between the two structures are shown.

INTRODUCTION

Okanoganite-(Y) is an unusual rare-earth borofluorosilicate first found by Boggs (1980) in mirolitic cavities of a peralkalic arfvedsonite-bearing granite from the Golden Horn batholith near Washington Pass, Okanogan County, U.S.A. Associated minerals are quartz, microcline, zircon, arfvedsonite, bastnaesite, zektzerite, astrophyllite, a pale green mica, and an unidentified Ca-REE mineral containing F. It was described as tan to pale-pink with a characteristic morphology due to twinning that simulates a tetrahedron. Boggs (1980) described the physical and chemical properties and determined the unit-cell dimensions using $hk0$ precession and $h0l$ Weissenberg photographs. The poor-quality diffraction data were inconclusive in defining the space group (a rhombohedral unit-cell was indicated by the observed absences $-h + k + l = 3n$). More recently, Ballirano et al. (2002) showed that the unit-cell dimensions and X-ray powder diffraction pattern of vicanite-(Ce) are similar to those of okanoganite-(Y), suggesting close similarities between the phases. Taking into account the data from Boggs (1980), they proposed a possible unit formula for okanoganite-(Y) that, owing to the absence of a structure refinement, could not be verified.

For these reasons, we undertook a crystal chemical study of okanoganite-(Y) and present the results here.

EXPERIMENTAL METHODS

Crystals of okanoganite-(Y) from the same locality (Boggs 1980) were provided by V. Mattioli, a keen collector of miner-

als. The matrix containing okanoganite-(Y) crystals consists of microcline + quartz; other minerals present are acmite, arfvedsonite, and zircon. The morphology and twinning of the crystals are the same as those observed by Boggs (1980) and only a few small fragments show perfect extinction and good X-ray diffraction quality. Diffraction data were collected using a Bruker-Axs Smart-Apex CCD-based diffractometer, and crystal data are reported in Table 1.

Intensity data for structure refinement (SREF) suggest the non-centrosymmetric space group $R3m$. The crystal structure was solved using the atomic parameters of vicanite-(Ce), allowing for the absence of As and a different choice of scattering factors at the M sites, as suggested by preliminary chemical analysis. Weighted full-matrix least-squares refinement on F was done using the program Crystals (Watkin et al. 2001); the Fe site was fixed at the origin. The structure-refinement results are shown in Table 2 (atom coordinates and U_{eq}) and Table 3¹ (U_{ij}); selected bond lengths and angles are given in Table 4. Observed and calculated structure factors are listed in Table 5¹.

The same crystal used for the structure refinement was embedded in epoxy resin, polished and analyzed with both electron- and ion-microprobes.

Electron microprobe (EMP) analysis was done with a Cameca SX 50 microprobe equipped with five WD spectrometers offering a combination of LiF, PET, TAP, PC1, and PC3 monochromators,

¹For a copy of Tables 3 and 5, Document item AM-04-069, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at <http://www.minsocam.org>.

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TABLE 1. Crystal data for okanoganite-(Y)

<i>a</i> (Å)	10.7108(5) Å
<i>c</i> (Å)	27.0398(11) Å
<i>V</i> (Å ³)	2686.5(3) Å ³
Space group	<i>R</i> 3 <i>m</i>
<i>Z</i>	3
Size (mm)	0.05 × 0.04 × 0.03
<i>D</i> _{calc} (g/cm ³)	4.96
<i>μ</i> (cm ⁻¹)	193.45
Detector type	Smart-Apex CCD plate
Scan type	<i>ω</i> scans
Scan width (°)	0.1
Scan time (s)	60
Abs. correction*	empirical
Total Ref.	10860
2 θ range (°)	2–60
Ref. with <i>I</i> _o > 10 σ (<i>I</i> _o) [†]	2676
<i>h</i> range	–15 → 15
<i>k</i> range	–15 → 15
<i>l</i> range	–37 → 37
<i>R</i> _{int}	0.060
Unique Ref.	2062
Obs. Ref. <i>F</i> _o > 3 σ (<i>F</i> _o)	1857
<i>R</i> _{obs}	0.0323
<i>R</i> _{all}	0.0376
<i>R</i> _w	0.0380
GoF	1.09
Flack parameter	0.085(12)

* SADABS software (Sheldrick 1996).

† Ref. used for unit-cell least-square refinement.

and one ED spectrometer, located at CNR-IGAG (Rome). Analytical conditions were 15 kV accelerating voltage and 15 nA current intensity, and a defocused beam of 10 μ m. The following standards were used: wollastonite (Si,Ca), magnetite (Fe), rutile (Ti), jadeite (Na), and apatite (P). Phosphorus was analyzed with a PET crystal, then checked by applying PHA (pulse-height analysis). Data were reduced using the Cameca PAP matrix-correction program (Pouchou and Pichoir 1991).

Secondary ion mass spectrometry (SIMS) was done with a Cameca IMS 4f ion microprobe installed at CNR-IGG (Pavia). The mount was gold-coated (~400 Å thickness) to minimize charge accumulation during the analysis. The procedures adopted were similar to those described in Ottolini and Oberti (2000). Secondary-ion intensities were detected at the following masses: 44 (Ca), 88 (Sr), 89 (Y), 133 (Cs), 137 (Ba), 139 (La), 140 (Ce), 141 (Pr), 146 (Nd), 149 (Sm), 163 (Dy), 167 (Er), and 174 (Yb). Eu and Gd signals were obtained by deconvolution of the secondary-ion mass spectrum at mass numbers 151, 154, 156, 158, and 162. Analysis of 1 (H), 7 (Li), 9 (Be), 11 (B), and 19 (F) was done on a different day to allow the crystal to degas at a vacuum of ~10⁻⁷ Pa with the proper H-reference samples in the dual specimen-holder inlet-chamber. ³⁰Si⁺ was used as the internal matrix reference for Li, Be, and B, and both ⁴⁴Ca⁺ and ³⁰Si⁺ were used as internal standards for the quantification of H and F. Analysis was done after 10 min bombardment at the same sites previously investigated for REE and other trace elements. To avoid any topographic effect due to the pre-existing craters, the crystal was polished smooth before analysis and then gold coated. Analyses of ⁴⁴Ca⁺, ²⁰⁸Pb⁺, ²³²Th⁺, and ²³⁸U⁺ were added

TABLE 2. Site multiplicity (mult), site occupancies, refined site-scattering (ss, electrons), fractional coordinates and equivalent isotropic atom-displacement parameters (*U*_{eq} × 10⁴, Å²) in okanoganite-(Y) (first line); features of the structural sites in vicanite-(Ce) are also reported (second line)

Site	mult	occupancy	ss	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
M1	9	0.72(2) Ce + 0.28 Y	52.6(3)	–0.1304(1)	0.1304(1)	–0.3183(1)	102(2)
		0.75 Ce + 0.25 Ca	48.5	–0.1319	0.1319	–0.3188	96
M2	9	0.75(2) Ce + 0.25 Y	52.3(3)	–0.1362(1)	0.1362(1)	0.1005(1)	124(2)
		0.74 La + 0.26 Ca	47.3	–0.1379	0.1379	0.0966	121
M3	9	0.59(1) Ca + 0.41 Y	27.7(3)	0.1157(1)	–0.1157(1)	–0.0988(1)	184(6)
		0.99 Ca + 0.01 Ce	20.3	0.1149	–0.1149	–0.0979	149
M4	9	0.71(1) Y + 0.29 Ca	33.6(3)	0.1214(1)	–0.1214(1)	0.4681(1)	124(4)
		0.98 Ca + 0.02 Ce	20.7	0.1303	–0.1303	0.4668	151
M5	9	0.87(1) Y + 0.13 Th	45.4(3)	0.1379(1)	–0.1379(1)	0.2201(1)	112(3)
		0.82 Th + 0.18 Ca	77.1	0.1413	–0.1413	0.2174	88
Fe	3	0.77(7) Fe + 0.23 Ti	25.1(3)	0	0	0	152(11)
		0.82 Fe + 0.18 Al	23.7	0	0	0	64
Si1	9	1 Si	14	0.1694(2)	–0.1694(2)	0.0442(1)	131(12)
		1 Si	14	0.1692	–0.1692	0.0431	87
Si2	9	1 Si	14	–0.1707(2)	0.1707(2)	–0.0402(1)	106(9)
		1 Si	14	–0.1701	0.1701	–0.0404	84
B1	9	1 B	5	–0.0791(8)	0.0791(8)	0.2921(4)	208(32)
		1 B	5	–0.0780	0.0780	0.2926	98
Si3 (As1)	3	0.4(3) Si + 0.6 P	14.6(3)	0	0	–0.2123(2)	151(14)
		0.77 As + 0.23 P	28.9	0	0	–0.2107	88
Na	3	1 Na	11	0	0	–0.4242(3)	267(25)
		0.58 Na	6.4	0	0	–0.4264	238
O1	9	1 O	8	0.0816(4)	–0.0816(4)	0.0469(3)	169(30)
		1 O	8	0.0821	–0.0821	0.0452	111
O2	9	1 O	8	0.1867(4)	–0.1867(4)	–0.0141(3)	172(32)
		1 O	8	0.1867	–0.1867	–0.0149	120
O3	18	1 O	8	0.3257(6)	–0.0667(6)	0.0708(2)	152(28)
		1 O	8	0.3233	–0.0680	0.0694	132
O4	9	1 O	8	–0.0835(4)	0.0835(4)	–0.0495(3)	171(28)
		1 O	8	–0.0837	0.0837	–0.0490	120
O5	9	1 O	8	–0.1909(4)	0.1909(4)	0.0188(3)	143(27)
		1 O	8	–0.1926	0.1926	0.0170	124
O6	18	1 O	8	–0.3312(6)	0.0791(7)	–0.0626(2)	229(30)
		1 O	8	–0.3277	0.0783	–0.0643	151
O7	9	1 O	8	0.0770(4)	–0.0770(4)	0.3062(3)	138(28)
		1 O	8	0.0761	–0.0761	0.3045	89
O8	9	1 O	8	–0.0957(4)	0.0957(4)	0.2388(3)	125(27)
		1 O	8	–0.0951	0.0951	0.2389	96
O9	9	1 OH	8	0.0832(5)	–0.0832(5)	0.1453(3)	202(28)
		1 O	8	0.0728	–0.0728	0.1443	135
O10	3	1 O	8	0	0	–0.1518(5)	254(35)
		1 O	8	0	0	–0.1491	161
O11	18	0.5 O	4	0.1550(13)	0.0470(15)	–0.2330(4)	314(37)
		0.5 O	4	0.1605	0.0460	–0.2332	191
F12	9	1 F	9	–0.0897(4)	0.0897(4)	–0.4885(2)	208(28)
		0.42 O + 0.58 F	8.6	–0.0812	0.0812	–0.4922	185
F13	3	1 F	9	0	0	–0.3390(5)	199(41)
		1 F	9	0	0	–0.3366	258
F14	18	1 F	9	0.0162(6)	0.3055(6)	–0.1607(2)	280(32)
		1 F	9	0.0212	0.3058	–0.1612	200
W	3	1 OH	8	0	0	0.4360(5)	188(38)
		0.21 H ₂ O	1.7	0	0	0.4350	200

Notes: The B2 and As2 site of vicanite-(Ce) are absent in okanoganite-(Y); esd are reported only for okanoganite-(Y).

later for completeness of the study. Standards that match the chemical composition of this sample do not exist. In the present study, we used apatite Snarum, britholite Los, NIST SRM 610, and LL St b (Ottolini and Oberti 2000; Oberti et al. 2001) for Sr, Y, REE, Ba, U, Pb, and Th. Cesium was tested at mass 133 (amu) but the content (ppm wt level) was insignificant in terms of the crystal-chemical formula. Quantification of Li, Be, and B was done following Ottolini et al. (1993). For Li, in addition, empirical corrections were done for the relative-to-Si ion yield for Li, IY(Li/Si), to take into account the different silica contents of our glassy standards relative to that of the sample. The overall accuracy was estimated as 5–15% for medium and heavy elements, and 5% for Li, Be, and B. The analysis of F by SIMS

TABLE 4. Selected bond distances (Å) and angles (°) in okanoganite-(Y) and vicanite-(Ce); only the atom sites occurring in okanoganite-(Y) are reported

	Okanoganite	Vicanite	Okanoganite	Vicanite
M1-O3 ×2	2.494 (5)	2.507	Fe-O1 ×3	1.975 (7)
M1-O5 ×2	2.540 (4)	2.558	Fe-O4 ×3	2.046 (8)
M1-O6 ×2	2.515 (6)	2.591	Mean	2.011
M1-O7	2.601 (8)	2.631		2.016
M1-O11	2.527 (11)	2.557	O1-Fe-O1 ×3	83.2(4)
M1-F13	2.482 (3)	2.517	O1-Fe-O4 ×6	97.4(2)
Mean	2.523	2.557	O4-Fe-O4 ×3	82.0(3)
M2-O1 ×2	2.636 (5)	2.652	Si1-O1	1.631 (4)
M2-O3 ×2	2.633 (5)	2.629	Si1-O2	1.609 (8)
M2-O5	2.432 (7)	2.402	Si1-O3 ×2	1.640 (5)
M2-O9 ×2	2.517 (3)	2.590	Mean	1.630
M2-O11	2.868 (15)	2.818		1.629
M2-F14 ×2	2.574 (5)	2.633	O1-Si1-O2	104.0(4)
Mean	2.602	2.623	O1-Si1-O3 ×2	106.5(3)
			O2-Si1-O3 ×2	111.7(2)
M3-O2	2.641 (8)	2.638	O3-Si1-O3	115.6(4)
M3-O4 ×2	2.337 (5)	2.345		115.4
M3-O6 ×2	2.947 (7)	2.922	Si2-O4	1.638 (4)
M3-O8	2.263 (8)	2.312	Si2-O5	1.636 (8)
M3-O10	2.583 (8)	2.567	Si2-O6 ×2	1.612 (6)
M3-F14 ×2	2.326 (5)	2.351	Mean	1.625
Mean	2.523	2.528		
			O4-Si2-O5	112.0(4)
M4-O3 ×2	2.306 (5)	2.336	O4-Si2-O6 ×2	109.5(3)
M4-O11	2.681 (12)	2.502	O5-Si2-O6 ×2	106.0(3)
M4-F12 ×2	2.339 (4)	2.410	O6-Si2-O6	113.8(5)
M4-F14 ×2	2.361 (5)	2.353		112.7
M4-W	2.415 (5)	2.591	B1-O2	1.452 (15)
Mean	2.389	2.391	B1-O7 ×2	1.497 (9)
			B1-O8	1.473 (13)
M5-O6 ×2	2.323 (6)	2.352	Mean	1.480
M5-O7	2.589 (7)	2.675		1.481
M5-O8 ×2	2.328 (2)	2.409	O2-B1-O7 ×2	107.8(6)
M5-O9	2.260 (7)	2.374	O2-B1-O8	108.2(10)
M5-F12	2.264 (7)	2.384	O7-B1-O7	111.4(11)
M5-F14 ×2	2.550 (6)	2.550	O7-B1-O8 ×2	110.7(6)
Mean	2.390	2.450		108.8
			Si3(As1)-O10	1.632 (15)
Na-O6 ×6	2.839 (7)	2.897	Si3(As1)-O11 ×3	1.578 (12)
Na-F12 ×3	2.407 (9)	2.355	Mean	1.592
Na-F13	2.306 (16)	2.454		1.671
Mean	2.656	2.690	O10-Si3-O11 ×3	110.8(4)
			O11-Si3-O11 ×3	108.1(4)
				107.2

was extremely demanding owing to the lack of a matrix-matched standard. Fluorine is a difficult element to investigate by EMPA and SIMS due to several kinds of matrix effects and artifacts (see Ottolini et al. 2000, and reference therein, for a general discussion). We used britholite Los and other low-silica reference materials as standards for H and F (estimated accuracy ~10% relative). Final chemical data (wt%) and unit formulae calculated on the basis of 38 O pfu, as suggested from the SREF study, are reported in Table 6, together with the refined mean site-scattering values and those calculated from the unit formula.

CRYSTAL STRUCTURE

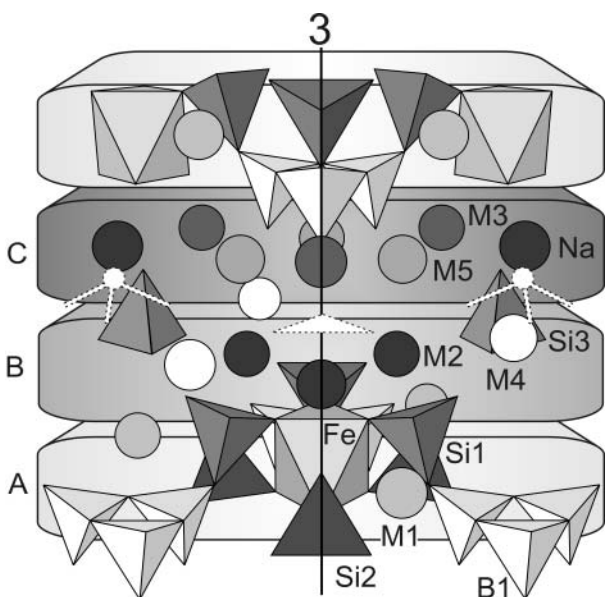
The structure of okanoganite-(Y) (Fig. 1) shows three distinct layers (A, B, C) along *c* (at intervals of ~1/9*c*) similar to those of vicanite-(Ce). Layer A (*z* ~ 0, 1/3, 2/3) is made up of the centric ^{VI}Fe(SiO₄)₆ group, the B₃O₃ ring, and the M1 polyhedra. Layer B (*z* ~ 1/9, 4/9, 7/9) contains the M2 and M4 polyhedra and an SiO₄ tetrahedron. Layer C (*z* ~ 2/9, 5/9, 8/9) consists of M3 and M5 polyhedra and the Na site. The names and positions of anions in the different layers are shown in Ballirano et al. (2002; Figs. 1, 2, and 3).

TABLE 6. Chemical analysis of okanoganite-(Y), unit formula calculated on the basis of 38 O, calculated (ssc) and observed (sso) site-scattering at the M + Na sites and at the Fe site

	Wt-%		Apfu
CaO	5.50	Ca	2.65
SrO	0.08	Sr	0.02
BaO	0.08	Ba	0.01
Y ₂ O ₃	18.94	Y	4.52
La ₂ O ₃	7.60	La	1.26
Ce ₂ O ₃	14.37	Ce	2.36
Pr ₂ O ₃	1.88	Pr	0.31
Nd ₂ O ₃	7.52	Nd	1.21
Sm ₂ O ₃	2.07	Sm	0.32
Eu ₂ O ₃	0.01	Eu	<0.01
Gd ₂ O ₃	2.69	Gd	0.40
Tb ₂ O ₃ *	0.48	Tb	0.07
Dy ₂ O ₃	3.23	Dy	0.47
Ho ₂ O ₃	n.a.	Ho	-
Er ₂ O ₃	1.88	Er	0.26
Tm ₂ O ₃ *	0.20	Tm	0.03
Yb ₂ O ₃	0.87	Yb	0.12
Lu ₂ O ₃	n.a.	Lu	-
PbO ₂	0.01	Pb	<0.01
UO ₂	0.08	U	0.01
ThO ₂	1.87	Th	0.19
Na ₂ O	1.87	Na	1.63
Fe ₂ O ₃	2.18	Σ M + Na	15.85
TiO ₂	0.56	Fe ³⁺	0.74
SiO ₂	14.94	Ti	0.19
Li ₂ O	0.02	Li	0.04
BeO	<0.01	Σ Fe	0.97
B ₂ O ₃	3.80	Si	6.71
P ₂ O ₅	0.83	Be	0.01
H ₂ O	1.33	B	2.94
F	7.07	P	0.32
-O = F	2.98	Σ T	9.98
Total	98.99	OH	3.98
		F	10.04
		Σ OH + F	14.02
	epfu		epfu
SSC _{ΣM+Na}	675.5	Sso _{ΣM+Na}	645.6
SSC _{ΣFe}	23.45	Sso _{ΣFe}	25.08

Note: n.a. = not analyzed.

* Tb₂O₃ and Tm₂O₃ data were obtained from Figure 2 by interpolation.

**FIGURE 1.** A simplified sketch of the okanoganite-(Y) structure; the sequence of layers along *c* are shown; the BO₃ triangle and the As³⁺O₃ pyramid [not present in okanoganite-(Y)] are drawn with dashed lines.

Polyhedra in the A layer: Fe, Si1, Si2, B1, M1

The Fe octahedron at (0 0 0) with $3m$ point symmetry is distorted: the three Fe-O1 distances (1.975 Å) are shorter than the three Fe-O4 distances (2.046 Å). The refined site scattering (25.1 electrons) and the mean bond-length (2.011 Å) confirm that the Fe and Ti of the unit formula occur entirely at this site. The SiO₄ and BO₄ tetrahedra are fairly regular; the mean bond distances are 1.630, 1.625, and 1.480 Å for Si1, Si2, and B1, respectively. As in vicanite-(Ce), the B1 tetrahedra are arranged in a threefold ring that, with three Si1 tetrahedra, forms the (Si₃B₃O₁₈)⁻¹⁵ polyanion. Three O1 corners of the polyanion link to three Fe sites that are connected to three Si2 tetrahedra via the O4 atoms. Layer A is completed by the ^[IX]M1 site [eight O and one F, <M1-O(F)> 2.523 Å] that contains a high concentration of REEs (site scattering = 52.6 electrons).

Polyhedra in the B layer: M2, M4, Si3

M2 bonds to 10 anions [eight O and two F, <M2-O(F)> 2.602 Å] and has site scattering (52.3 electrons) similar to that of M1. The M4 site has a lower electron density (33.6 electrons) and bonds to eight anions [four O and four F; <M4-O(F)(W)> 2.389 Å]. The Si3 tetrahedron shares corners with M2 and M4 and shows three short bond distances. The refined <Si3-O> distance of 1.592 Å is somewhat short for an SiO₄ tetrahedron but in accord with the occurrence of some P at this site. The Si3 site shows the same crystallographic features as the As1 site of vicanite-(Ce) (i.e., it occurs at the center of a tetrahedron in two orientations with the same probability of occurrence).

Polyhedra in the C layer: M3, M5, Na

The M3 site is nine-coordinated [seven O and two F, <M3-O(F)> 2.523 Å] and has the lowest refined electron density (27.7 electrons); it has a greater content of Ca than other M sites. The M5 site bonds to nine anions [six O and three F, <M5-O(F)> 2.390 Å] and has an electron density equal to the average of all M sites (45.4 electrons). Bond-valence analysis (Table 7) suggests that the small amount of Th in okanoganite-(Y) occurs at this site. The Na site is completely filled by Na and is ten-coordinated [six O and four F, <Na-O(F)> 2.656 Å].

Connections between polyhedra from different layers

Most of the linkages between layers involve the M polyhedra. M1 in layer A shares faces with both M2 and M4 in layer B, and shares faces with M5 and Na polyhedra in the underlying C layer. There is no face sharing between the B and C layers. Edges shared between M polyhedra and numerous corner linkages involving low-coordination polyhedra produce additional connections along *c*.

DISCUSSION

Comparison between okanoganite-(Y) and vicanite-(Ce) structures

The okanoganite-(Y) structure is strongly related to that of vicanite-(Ce). The two minerals show the same sequence of layers along *c*, resulting in fairly similar lattice constants. The main difference is the absence of some structural sites in okanoganite-(Y) that occur in vicanite-(Ce).

The As1 tetrahedron, occupied by As and P in vicanite-(Ce), is filled by Si + P (and named Si3) in okanoganite-(Y). The As2 pyramid is absent in okanoganite-(Y), which allows complete occupancy of the Na site; of course, the disordered part of the vicanite-(Ce) structure (As2 pyramids and Na polyhedra statistically disordered and mutually exclusive) is absent in okanoganite-(Y). Boron is present in both minerals, but in okanoganite-(Y), it occurs only at the tetrahedral B1 site. During the first cycles of refinement, with B placed at the triangular B2 site, an abnormally high atom-displacement factor was observed and any attempt to refine the site scattering failed.

These two borosilicates show different cation populations at the M sites. In vicanite-(Ce), M3 and M4 are occupied by Ca, M5 by Th, and M1 and M2 are mainly filled by REE. In okanoganite-(Y), the lower amount of Ca (CaO 5.5 wt%) precludes the presence of exclusively Ca-filled M sites. However, the results indicate that Ca is preferentially located at M3 and M4 (lowest site-scattering) and Th at M5 (charge > 3 v.u.), as in vicanite-(Ce).

The SIMS data show the presence of both F and H₂O in okanoganite-(Y) and bond-valence analysis was used to distin-

TABLE 7. Bond valence analysis (v.u.) of okanoganite-(Y)

Site	M1	M2	M3	M4	M5	Fe	Si1	Si2	B1	Si3	Na	Total
Atom type	Y _{0.28} Ce _{0.72}	Y _{0.25} Ce _{0.75}	Ca _{0.59} Y _{0.41}	Ca _{0.29} Y _{0.71}	Y _{0.87} Th _{0.13}	Fe _{0.77} Ti _{0.23}	Si	Si	B	Si _{0.7} P _{0.3}	Na	
Site charge	3.00	3.00	2.41	2.71	3.13	3.23	4	4	3	4.30	1	
O1		↓ ² 0.25 ^{2→}				↓ ³ 0.58	1.00					2.08
O2			0.17				1.06		0.83			2.06
O3	↓ ² 0.35	↓ ² 0.25		↓ ² 0.44			↓ ² 0.97					2.01
O4			↓ ² 0.39 ^{2→}			↓ ³ 0.48		0.95				2.21
O5	↓ ² 0.32 ^{2→}	0.43						0.96				2.02
O6	↓ ² 0.34		↓ ² 0.08		↓ ² 0.46			↓ ² 1.03			↓ ⁶ 0.06	1.97
O7	0.26				0.23				↓ ² 0.72 ^{2→}			1.93
O8			0.49		↓ ² 0.46 ^{2→}				0.73			2.14
O9		↓ ² 0.34 ^{2→}			0.54							1.22
O10			0.21 ^{3→}							0.95		1.58
O11	0.33	0.13		0.17						↓ ³ 1.08		1.71
F12				↓ ² 0.30 ^{2→}	0.41						↓ ³ 0.14	1.15
F13	0.27 ^{3→}										0.19	0.97
F14		↓ ² 0.22	↓ ² 0.30	↓ ² 0.28	↓ ² 0.19							0.99
(W)				0.33 ^{3→}								0.99
Total	2.88	2.68	2.41	2.54	3.40	3.18	4.00	3.97	3.00	4.19	0.97	

Notes: the valence of each site takes account of the contribution of different atom species; bond valence calculated after Brown and Altermatt (1985) with the parameters given by Brese and O'Keefe (1991).

guish between O^{2-} , $(OH)^-$ or F, and H_2O . Table 7 shows a charge close to 1 v.u. for all anion sites not involved in low-coordination polyhedra (O9, F12, F13, F14, and W). These sites correspond to 14 anions pfu, in agreement with the number of monovalent anions reported in the unit formula ($10F + 4OH$). Attempts to refine the mean atomic number at the monovalent-anion sites showed values closer to 8 at the O9 (multiplicity 3) and W sites (multiplicity 1). The W site, only partly occupied in vicanite-(Ce), is completely filled in okanoganite-(Y) (W was assumed to be H_2O by Ballirano et al. 2002). In conclusion, the four H of the unit formula correspond to four OH groups at the O9 and W sites, and the ten F atoms occur at the other anion sites bonded to the largest cations: F12 (multiplicity 3), F13 (multiplicity 1), and F14 (multiplicity 6).

REE pattern of okanoganite-(Y)

In Figure 2, we show the C1-chondrite REE pattern (normalization factors from Anders and Grevesse 1989) for the crystal studied here. The pattern is rather flat for all REE, except for Eu, that shows a very pronounced negative anomaly ($Eu/Eu^* = 0.009$), which is presumably controlled by the associated microcline. Owing to the smooth pattern shape, the concentrations of other REE, such as Tb and Tm (not included in our analytical mass-acquisition list) can be estimated by interpolation (Table 6). In the C/C1 pattern, Y is generally placed between Dy and Er, due to the similarity of its ionic radius (IXY 1.075 Å) to that of Ho ($IXHo$ 1.072 Å; Shannon 1976). In Figure 2, we have plotted for comparison the corresponding C/C1 distribution from the okanoganite-(Y) of Boggs (1980). We may observe that: (1) the REE concentrations are very similar, especially in the LREE region (La, Ce, Pr), although Eu is missing in the data from Boggs (1980); (2) the scatter in the medium and heavy REE region in the

Boggs (1980) crystal is presumably related to some problems in the EMPA correction/background-subtraction procedures.

Classification

Okanoganite-(Y) and vicanite-(Ce) are nesoborosilicates characterized by the $(Si_3B_3O_{18})^{15-}$ polyanion, and their simplified formulae (Table 8) highlights the similarity between the two minerals. They can be classified as *mixed-oxyanion borates* (Hawthorne et al. 1996) considering that the $(Si_3B_3O_{18})^{15-}$ polyanion consists of a three-membered ring of BO_4 tetrahedra linked to isolated SiO_4 tetrahedra. Interestingly, the only two minerals reported in this class and characterized by a structural unit with a three-membered ring (howlite and garrelsite) are formed by $1\Delta 2\Box$, and okanoganite-(Y) and vicanite-(Ce) are the only borosilicate minerals characterized by $3\Box$ rings.

The complete unit formula of okanoganite-(Y) has been obtained by EMP and SIMS analyses (Table 6), and is in accord with SREF results. The discrepancy between the refined site-scattering at the $15 + 1$ cation sites [645.6(4) electrons pfu] and the mean atomic number for these sites (675.5 electrons) is 4.6%, within the overall analytical uncertainty of the EMPA + SIMS analyses.

Relative to the unit formula of Boggs (1980) calculated on the basis of 16 large cations, $[Y_{4.9}REE_{7.1}Na_{2.4}Ca_{1.6}\Sigma_{16.0}(Fe,Ti)_{0.8}Si_{6.5}B_{2.4}O_{31}F_{16}]$, the main differences involve the low B content, the absence of P and OH (or H_2O), the amount of Na and Ca, and the very high F content. We can make some hypotheses: (1) the low B content (2.4 instead of 3 atoms pfu) may be due to problems with the analytical technique (spectrophotometry); (2) the amount of Si is similar, but in the earlier study P is absent; we detected P in our okanoganite-(Y) and its presence at the Si3 site is supported by geometrical and physical considerations (i.e., the bond

TABLE 8. Simplified crystal-chemical formula of okanoganite-(Y) (first line) and vicanite-(Ce) (second line)

(REE, Y, Ca, Na) ₁₅	(Fe ³⁺)	(SiO ₄) ₃	(Si ₃ B ₃ O ₁₈)	(OH) ₃	(SiO ₄)	(-)	(NaF ₃)	F ₇	(OH)
(Ca, REE, Th) ₁₅	(Fe ³⁺)	(SiO ₄) ₃	(Si ₃ B ₃ O ₁₈)	(BO ₃)	(As ⁵⁺ O ₄)	(As ⁵⁺ O ₃) _x	(NaF ₃) _{1-x}	F ₇	•0.2(H ₂ O)

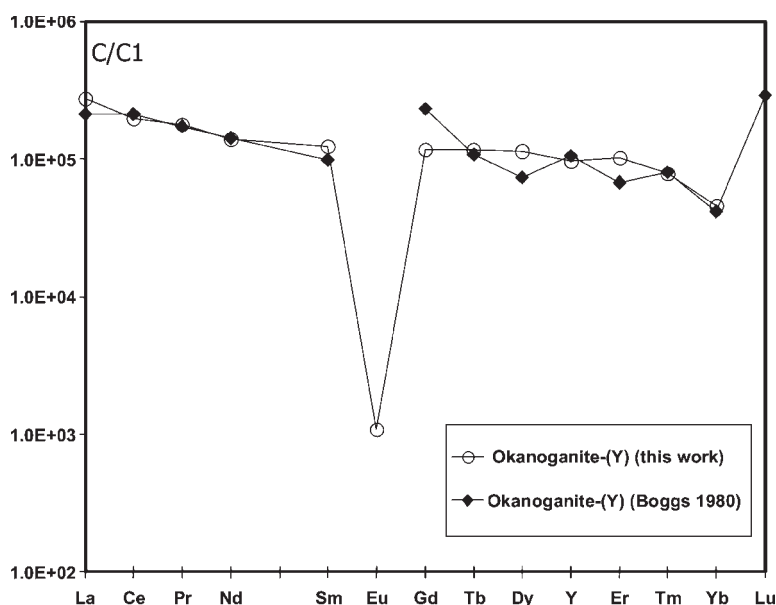


FIGURE 2. Chondritic REE patterns for the okanoganite-(Y) sample of this work and for the sample studied by Boggs (1980).

lengths, site scattering, and charge); (3) the Na/Ca ratio from the unit formula in the earlier study (1.5) is much higher than in our crystal (~0.6) and the F content is very different (~16 atoms pfu vs. 10.04 in the present work).

The presence of other F-rich phases in the miarolitic cavity [e.g., bastnaesite-(Ce) (~9 wt% F), polyolithionite (~4.8 wt% F), gagarinite (29.4 wt% F), and fluorite (48.6 wt% F)] suggests competition for F among these minerals. However, only 14 anion sites pfu (not bonded to low-coordination polyhedra) can host monovalent anions, and the F content cannot exceed 14 atoms pfu in the most F-rich okanoganite-(Y) crystals.

ACKNOWLEDGMENTS

Thanks are due to F. Mazzi (University of Pavia) for fruitful discussions during the preparation of the manuscript. The authors are grateful to S. Merlini and F.C. Hawthorne for their reviews that greatly improved and clarified the manuscript, and to the Associate Editor S. Quartieri. We also thank M. Serracino from the Istituto di Geologia Ambientale e Geoingegneria (IGAG) - CNR, Rome, for assistance with EMPA. The Italian CNR is acknowledged for financing the ion microprobe at the Istituto di Geoscienze e Georisorse (IGG), Pavia.

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MANUSCRIPT RECEIVED JANUARY 29, 2004

MANUSCRIPT ACCEPTED APRIL 2, 2004

MANUSCRIPT HANDLED BY SIMONA QUARTIERI