

The crystal structure of vicanite-(Ce), a borosilicate showing an unusual $(\text{Si}_3\text{B}_3\text{O}_{18})^{15-}$ polyanion

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ABSTRACT

The crystal structure of holotype vicanite-(Ce) has been solved and refined to $R = 1.8\%$ for 1398 observed reflections with the aid of a new crystal from the same locality (Tre Croci, Vetralla, Italy), found more than 10 years after the first. The new unit formula is $(\text{Ca,REE,Th})_{15}\text{Fe}^{3+}(\text{SiO}_4)_3(\text{Si}_3\text{B}_3\text{O}_{18})(\text{BO}_3)(\text{As}^{5+}\text{O}_4)(\text{As}^{3+}\text{O}_3)_x(\text{NaF}_3)_{1-x}\text{F}_7 \cdot 0.2\text{H}_2\text{O}$ with $x = 0.4$. The structure is trigonal, $R3m$, $Z = 3$, $a = 10.8112(2)$, $c = 27.3296(12)$ Å, and layered along [001] with three distinct layers.

Layer A at z ca. 0 (1/3, 2/3) contains an $\text{Fe}(\text{SiO}_4)_6$ group and a threefold B_3O_9 borate ring. Each tetrahedron of the ring shares one oxygen atom with one Si tetrahedron, forming an unusual $\text{Si}_3\text{B}_3\text{O}_{18}^{15-}$ polyanion.

Layer B at z ca. 1/9 (4/9, 7/9) contains an AsO_4 tetrahedron and a BO_3 triangle.

Layer C at z ca. 2/9 (5/9, 8/9) represents the disordered part of the structure, containing two very close (0.85 Å) $\text{As}^{3+}\text{O}_3^{3-}$ and NaF_3^- polyhedra, the occurrence of which is mutually exclusive and statistically disordered.

A 3-dimensional network of $\text{M}(\text{O,F})_n$ polyhedra ($\text{M} = \text{Ca, REE, Th}$; $8 < n < 10$) provide connections among neighboring layers.

INTRODUCTION

Vicanite-(Ce) has been described as a new mineral from the Vico volcanic complex, found at Tre Croci, Vetralla (Latium, Italy) by Maras et al. (1995). In association with other Th-U-REE-bearing minerals, it occurs as tiny euhedral crystals inside small miarolitic cavities in ejecta of syenitic composition. Maras et al. (1995) report the formula, on the basis of 47 (O + F), as:

$(\text{Ca}_{8.03}\text{Ce}_{2.32}\text{La}_{1.95}\text{Th}_{1.82}\text{Pr}_{0.44}\text{Nd}_{0.28}\text{U}_{0.19})_{15.03}(\text{As}_{0.86}^{5+}\text{P}_{0.14})_{1.00}(\text{As}_{0.34}^{3+}\text{Na}_{0.12})_{0.46}(\text{Fe}_{0.57}^{3+}\text{Ti}_{0.05}\text{Al}_{0.08})_{0.70}\text{Si}_{6.07}\text{B}_{4.00}(\text{O}_{36.58}\text{F}_{10.42})_{47}$. Further details, particularly the calculation of As^{3+} and As^{5+} , may be found in the original reference. This formula is in partial agreement with the simplified formula derived from a preliminary crystal-structure determination: $(\text{Ca,REE,Th})_{15}\text{As}^{5+}(\text{As}_{0.5}^{3+}\text{Na}_{0.5})\text{Fe}^{3+}\text{Si}_6\text{B}_4\text{O}_{40}\text{F}_7$. (Callegari et al. 1991). According to its cell parameters, vicanite-(Ce) is closely related to okanoganite (Boggs 1980), a REE borofluorosilicate from Okanogan County, Washington.

EXPERIMENTAL METHOD

Two different crystals from the same locality were used for crystallographic study at Pavia (*a*) and Rome (*b*). Crystal *a* represents the holotype of this mineral species, whereas crystal *b* was found more than ten years later. Details on collection of X-ray data and least-squares refinements of the crystal structure are given in Table 1.

Crystal *a*

The transparent yellowish-green crystal of vicanite-(Ce) selected for single-crystal work was almost isometric. Data were collected on a Philips PW1100 automated diffractometer using graphite monochromatized $\text{MoK}\alpha$ radiation. Intensities were corrected for Lorentz and polarization factors and for absorption following the empirical method of North et al. (1968). Unit-cell dimensions were calculated from least-squares refinement of the d -values of the reflections obtained from 60 rows of the reciprocal lattice. The acentric space group $R3m$ was unequivocally determined from systematic absences and statistical evaluation of the intensities of the reflections. The crystal structure was solved by preliminary inspection of the Patterson synthesis, followed by those of subsequent F-Fourier maps. Refinement of the crystal structure was performed with a locally written program: unitary weights for the structure factors and scattering factors for neutral atoms were used. Refinement was carried out applying anisotropic displacement factors to all atoms, with the exclusion of the W (water) oxygen atom. The final R -factor was 1.8% for 1398 observed reflections with $I/\sigma(I) > 3$ and 2.2% for all 1571 unique reflections with $l \geq 0$ in space group $R3m$; these results take anomalous scattering into account.

Crystal *b*

Under crossed polars, the crystal was identified as twinned, and a small fragment from one of the twins was cut and selected for X-ray data collection. Refined cell parameters were derived from a least-squares procedure on 50 reflections ($15^\circ < 2\theta < 30^\circ$). A psi-scan empirical absorption correction was

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TABLE 1. Summary of X-ray and structure refinement data for crystals *a* and *b*

Formula unit	(Ca, REE, Th) ₁₅ Fe ³⁺ (SiO ₄) ₃ (Si ₃ B ₃ O ₁₈)(BO ₃) (As ^{±5} O ₄) (As ^{±3} O ₃) _x (NaF ₃) _{1-x} F ₇ ·0.2H ₂ O <i>x</i> = 0.4	
Crystal	<i>a</i>	<i>b</i>
Space group	<i>R</i> 3 <i>m</i>	<i>R</i> 3 <i>m</i>
<i>Z</i>	3	3
<i>a</i> (Å)	10.8112(4)	10.8194(5)
<i>c</i> (Å)	27.3205(12)	27.3354(22)
Diffractometer	Philips PW 1100	Siemens P4
Radiation	Mo <i>K</i> α	Mo <i>K</i> α
Crystal size (mm)	0.18 × 0.20 × 0.24	0.2 × 0.3 × 0.3
Scan mode	ω	ω
Scan width (°)	1.0	1.0
Scan speed (°/s)	0.05	0.05
2θ _{max} (°)	70	70
<i>N</i> _{meas}	8117(± <i>h</i> , ± <i>k</i> , ± <i>l</i>)	3066 (+ <i>h</i> , + <i>k</i> , ± <i>l</i>)
<i>N</i> _{unique}	1571	3066
<i>N</i> _{obs} [<i>I</i> σ(<i>I</i>) > <i>x</i>]	1398 <i>x</i> = 3	1394 <i>x</i> = 4
No. of refined parms	162	162
<i>R</i> (%)	1.76	3.18
<i>wR</i> ² (%)	—	7.75

carried out. Neutral scattering curves were used throughout the refinement; in particular, the scattering curve of Ce was used to model the contribution of all REE elements. Starting positional parameters were those of crystal *a*. Anisotropic refinement, carried out using full-matrix least-squares techniques on *F*² (SHELXL-97; Sheldrick 1997), converged to a conventional *R* value of 3.2% for 1394 observed reflections with *I*/*σ*(*I*) > 4.

DESCRIPTION OF THE CRYSTAL STRUCTURE OF VICANITE-(Ce)

Atomic coordinates, site occupancies and isotropic displacement parameters are listed in Table 2 and bond distances in Table 3. Bond valences (Brown and Altermatt 1985; Brese and O'Keeffe 1991) are shown in Table 4. Anisotropic displacement parameters are listed in Table 5¹ and observed and calculated structure factors in Table 6¹.

The structure of vicanite-(Ce) consists of three distinct layers:

Layer A at *z* ca. 0 (1/3, 2/3) (Fig. 1) consists of an Fe(SiO₄)₆ group and a threefold B₃O₃ borate ring. The FeO₆ octahedron shares its oxygen atoms with six SiO₄ groups, three Si1 and three Si2. Each B1 tetrahedron of the borate ring shares one O2 oxygen atom with one Si1 tetrahedron, thus forming an unusual Si₃B₃O₁₈¹⁵⁻ polyanion. Each of these polyanions is connected by the O1 corners of the Si1 tetrahedra to three Fe octahedra, whereas each Fe octahedron shares three O1 corners with three polyanions and the remaining O4 corners with three Si2 tetrahedra. The M1-(O,F)₉ polyhedra interconnect layer A and layers B and C. The M1 site is occupied by rare earth elements (REE) and Ca, and is surrounded by nine oxygen atoms (two O3, two O5, two O6, O7, two O11) and one fluorine atom (F13); however, only one of the two O11 atoms is statistically present

(see below), because of the occurrence of short contact distances.

Layer B at *z* ca. 1/9 (4/9, 7/9) (Fig. 2) consists of As1 tetrahedra and B2 triangles linked via M2-(O,F)₁₀ and M4-(O,F)₈ polyhedra. Moreover, the latter two polyhedra provide connections with layers A and C. Each As1 tetrahedron is surrounded by six alternating M2-(O,F)₁₀ and M4-(O,F)₈ polyhedra, whereas each B2 triangle is coordinated by three M2-(O,F)₁₀ polyhedra. Like M1 site, the REE and Ca (26%) also fill M2 site. It coordinates eight oxygen atoms (two O1, two O3, O5, two O9, O11) and two F14 fluorine atoms. The M4 site is almost completely occupied by Ca. It coordinates six oxygen atoms (two O3, O11, two OF12, W) and two F14 fluorine atoms. This coordination is to some extent more complicated because OF12 and W occupy the disordered part of the crystal structure: oxygen fills nearly 40% of site OF12 together with 60% fluorine (see below), and the oxygen atom of one water molecule occupies only 21% of site W. According to occupancy refinement, the As1 tetrahedron is occupied by 0.77 As and

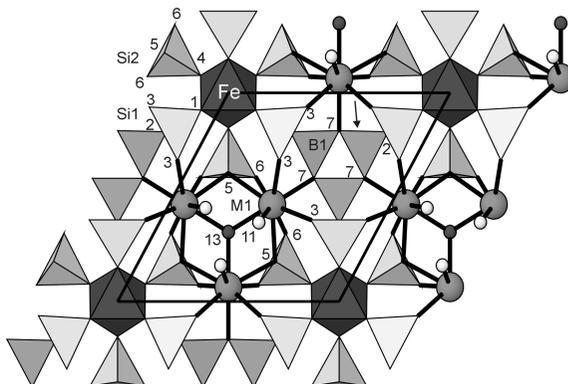


FIGURE 1. Layer A. Projection along [001] of a slab of the vicanite-(Ce) structure at *z* ca. 0. Arrow: O8 of B1 tetrahedron pointing down.

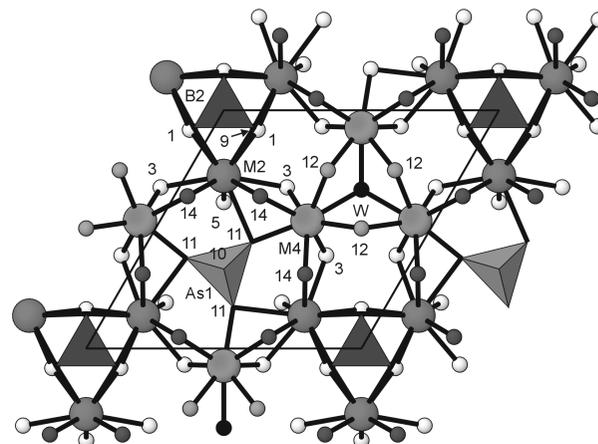


FIGURE 2. Layer B. Projection along [001] of a slab of the vicanite-(Ce) structure at *z* ca. 1/9.

¹For a copy of Tables 5 and 6, document item AM-02-012, 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>.

TABLE 2. Fractional coordinates, site occupancies, and isotropic displacement parameters in vicanite-(Ce)

Atoms	Site multiplicity	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (×10 ⁴)
M1	9	0.751(4)Ce;0.249Ca	-0.13188(3)	0.13188(3)	-0.31881(4)	96(2)
M2	9	0.738(4)La;0.262Ca	-0.13794(3)	0.13794(3)	0.09655(4)	121(2)
M3	9	0.992(3)Ca;0.008Ce	0.11490(9)	-0.11490(9)	-0.09790(7)	149(5)
M4	9	0.983(3)Ca;0.017Ce	0.13025(9)	-0.13025(9)	0.46683(7)	151(5)
M5	9	0.816(2)Th;0.184Ca	0.14125(2)	-0.14125(2)	0.21736(4)	88(1)
Fe	3	0.823(20)Fe;0.177Al	0	0	0	64(5)
Si1	9	1	0.1692(1)	-0.1692(1)	0.0431(1)	87(5)
Si2	9	1	-0.1701(1)	0.1701(1)	-0.0404(1)	84(5)
B1	9	1	-0.0780(4)	0.0780(4)	0.2926(3)	98(21)
B2	3	1	0	0	0.1467(6)	156(36)
As1	3	0.773(9)As;0.227P	0	0	-0.2107(1)	88(3)
As2	3	0.417(9)As	0	0	-0.4576(1)	74(7)
Na	3	0.583(9)Na	0	0	-0.4264(5)	238(31)
O1	9	1	0.0821(3)	-0.0821(3)	0.0452(2)	111(15)
O2	9	1	0.1867(3)	-0.1867(3)	-0.0149(2)	120(16)
O3	18	1	0.3233(4)	-0.0680(4)	0.0694(2)	132(13)
O4	9	1	-0.0837(3)	0.0837(3)	-0.0490(2)	120(15)
O5	9	1	-0.1926(3)	0.1926(3)	0.0170(2)	124(15)
O6	18	1	-0.3277(5)	0.0783(5)	-0.0643(2)	151(13)
O7	9	1	0.0761(3)	-0.0761(3)	0.3045(2)	89(14)
O8	9	1	-0.0951(3)	0.0951(3)	0.2389(2)	96(14)
O9	9	1	0.0728(3)	-0.0728(3)	0.1443(2)	135(17)
O10	3	1	0	0	-0.1491(4)	161(24)
O11	18	0.5 O	0.1605(9)	0.0460(9)	-0.2332(3)	191(31)
OF12	9	0.417O;0.583F	-0.0812(3)	0.0812(3)	-0.4922(2)	185(17)
F13	3	1	0	0	-0.3366(5)	258(28)
F14	18	1	0.0212(4)	0.3058(4)	-0.1612(2)	200(14)
W	3	0.21(5)	0	0	0.435(2)	200(150)

0.23 P. This tetrahedron shows two distinct configurations with the same statistical probability, due to the double multiplicity of the general position occupied by the O11 oxygen atom with respect to that of expected *m* symmetry. The last polyhedron of the B layer is a BO₃ triangle showing three equivalent B-O distances of 1.365(4) Å.

Layer C at *z* ca. 2/9 (5/9, 8/9) (Fig. 3) contains the disordered part of the structure: two very close (0.85 Å) As2 and Na sites and their polyhedra. Because of the short distance between these sites, their occurrence is mutually exclusive and statistically disordered: refinement results gave occupancies of 0.42 for As2 and 0.58 for Na. Similar occupancies were observed for oxygen and fluorine in OF12 during the first refinement cycles, suggesting the formation of two kinds of clusters: AsO₃³⁻ with O12, and NaF₃³⁻ with F12, according to the presence of one of the two cations. In the successive least-squares cycles, As occupancy in As2 and O occupancy in OF12 were constrained to be equal.

Site As2 coordinates three oxygen atoms at the corners of a triangle and its position is 0.95 Å out of the plane of the triangle. The peculiarity of this coordination (ψ -tetrahedron), as well as the lengths of the three equivalent As2-O12 bond distances (1.791 Å), easily identified the cation in As2 site as trivalent arsenic. The M3 site is completely occupied by Ca and thus the REE are practically absent (0.8%). It coordinates seven oxygen atoms (O2, two O4, two O6, O8, O10) and two F14 fluorine atoms. According to refinement of the occupancies, the M5 site contains 82% Th; the remaining part of the site was assigned to Ca, to adjust the total amount of this cation to the results of chemical analysis. The M5 site coordinates seven oxygen atoms (two O6, O7, two O8, O9, OF12) and two F14 fluorine atoms. A feature of the crystal structure of vicanite-

TABLE 3. Bond distances (Å) in vicanite-(Ce)

M1-O3 ×2	2.507 (4)	Fe-O1 ×3	1.972 (4)
M1-F13	2.517 (3)	Fe-O4 ×3	2.061 (5)
M1-O11	2.557 (9)	Mean	2.016
M1-O5 ×2	2.558 (3)		
M1-O6 ×2	2.591 (4)	Si1-O2	1.618 (6)
M1-O7	2.631 (4)	Si1-O1	1.632 (4)
Mean	2.557	Si1-O3 ×2	1.633 (5)
		Mean	1.629
M2-O5	2.402 (5)		
M2-O9 ×2	2.590 (5)	Si2-O6 ×2	1.620 (5)
M2-O3 ×2	2.629 (4)	Si2-O5	1.624 (6)
M2-F14 ×2	2.633 (4)	Si2-O4	1.635 (4)
M2-O1 ×2	2.652 (4)	Mean	1.625
M2-O11	2.818 (10)		
Mean	2.623	M3-O8	2.312 (3)
		M3-O4 ×2	2.345 (5)
M3-O8	2.312 (3)	M3-F14 ×2	2.351 (5)
M3-O4 ×2	2.345 (5)	M3-O10	2.567 (7)
M3-F14 ×2	2.351 (5)	M3-O2	2.638 (5)
M3-O10	2.567 (7)	M3-O6 ×2	2.922 (5)
M3-O2	2.638 (5)	Mean	2.528
M3-O6 ×2	2.922 (5)		
Mean	2.528	M4-O3 ×2	2.336 (4)
		M4-F14 ×2	2.353 (4)
M4-O3 ×2	2.336 (4)	M4-OF12 ×2	2.410 (4)
M4-F14 ×2	2.353 (4)	M4-O11	2.502 (10)
M4-OF12 ×2	2.410 (4)	M4-W(0.21)	2.591 (20)
M4-O11	2.502 (10)	Mean	2.391
M4-W(0.21)	2.591 (20)		
Mean	2.391	M5-O6 ×2	2.352 (5)
		M5-O9	2.374 (6)
M5-O6 ×2	2.352 (5)	M5-OF12	2.384 (4)
M5-O9	2.374 (6)	M5-O8 ×2	2.409 (4)
M5-OF12	2.384 (4)	M5-F14	2.550 (4)
M5-O8 ×2	2.409 (4)	M5-F13	2.454 (19)
M5-F14	2.550 (4)	M5-O7	2.675 (5)
M5-F13	2.454 (19)	Mean	2.451
M5-O7	2.675 (5)		
Mean	2.451	As2-O12 ×3	1.791(5)
		Na-F12 ×3	2.355 (11)
		Na-O6 ×6	2.897 (6)
		Mean	2.69

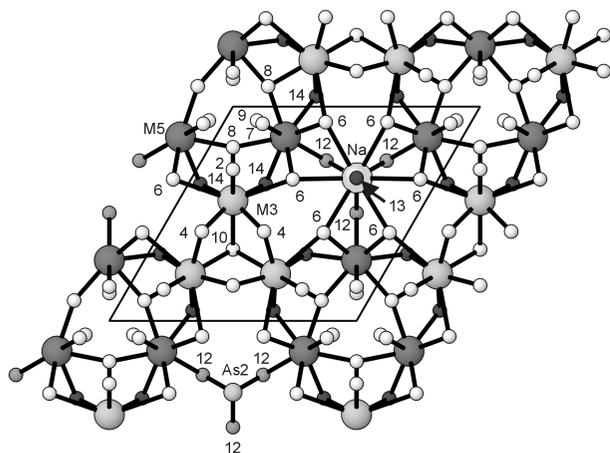


FIGURE 3. Layer C. Projection along [001] of a slab of the vicanite-(Ce) structure at z ca. $2/9$. For sake of clarity, Na and As polyhedra are drawn separately at $x = 1/3$, $y = 2/3$ and respectively at $x = 4/3$, $y = 2/3$.

(Ce) is the 3-dimensional network formed by the connections among the M polyhedra: each of them alternately shares faces, edges, or corners with one or, more commonly, two of all M1 to M5 polyhedra.

COMPARISON OF VICANITE-(Ce) AND OKANOANITE

Vicanite-(Ce) is structurally related to okanoganite (Boggs 1980): although their lattice constants and X-ray powder dif-

fraction patterns are similar, the most evident differences are in chemical composition. Significant quantities of Y are present in okanoganite, As and Th are absent, and Ca is significantly lower, whereas Na is higher than in vicanite-(Ce). Because of the absence of As, it is reasonable to presume that, in okanoganite, the Na polyhedron occupies the entire disordered part of the structure of vicanite-(Ce), in which the arsenite polyhedron is also present. Taking this into account, we recalculated the unit formula of okanoganite from the chemical analysis of Boggs (1980) on the basis of $15 + 1$ large cations, obtaining $(Y_{4.9}, REE_{7.1}, Na_{2.4}, Ca_{1.6})_{16.0}(Fe, Ti)_{0.8}Si_{6.5}B_{2.4}O_{31}F_{16}$.

Apart from the small amount of B found in okanoganite (2.4 instead of 4 atoms), due perhaps to difficulty in analysing by spectrophotometry, and the absence of As, the remaining part of the unit formula resembles that of vicanite-(Ce). Silicon (6.5 atoms) is high when compared with vicanite-(Ce) (6), but it is lower than 7 atoms. This is the Si content obtained if the arsenate tetrahedron in vicanite-(Ce) is replaced by a Si tetrahedron in okanoganite. Furthermore, if two M sites are filled predominantly by Y and two other M sites by the REE, Ca, and the residual Na from the occupancy of the Na site should be in the fifth M site. We tried to calculate the theoretical X-ray powder diffraction pattern with various distributions of Y, REE and (Na, Ca) in the five different M sites. The best agreement with the powder diffraction intensities reported by Boggs (1980) was obtained with REE in M1 and M2, (Na, Ca) in M4, and Y in M3 and M5 sites. Accordingly, the site populations in M1, M2 and M4 (layers A and B of the crystal structure) would practically be the same as in vicanite-(Ce), whereas in layer C, six Y^{3+} would replace both three Ca^{2+} in M3 and three Th^{4+} in M5 (Table 7).

TABLE 4. Bond valence analysis of vicanite-(Ce)

Site	M1	M2	M3	M4	M5	Fe	Si1	Si2	B1	B2	As1	As2	Na	Total
Atom type	Ce _{0.75} Ca _{0.25}	La _{0.74} Ca _{0.26}	Ca	Ca	Th _{0.82} Ca _{0.18}	Fe + Al	Si	Si	B	B	As ⁵⁺ + P	As ³⁺ _{0.42}	Na _{0.58}	
Formal charge	2.75	2.74	2	2	3.64	3	4	4	3	3	5	1.26	0.58	
O1		↓×2 _{0.24} ^{×2}				↓×3 _{0.54}	0.98							2.00
O2			0.16				1.02		0.77					1.95
O3	↓×2 _{0.34}	↓×2 _{0.26}		↓×2 _{0.37}			↓×2 _{0.98}							1.95
O4			↓×2 _{0.36} ^{×2}			↓×3 _{0.42}		0.97						2.11
O5	↓×2 _{0.30} ^{×2}	0.47						1.00						2.07
O6	↓×2 _{0.27}		↓×2 _{0.07}		↓×2 _{0.57}			↓×2 _{1.01}					↓×6 _{0.04}	1.96
O7	0.24				0.24				↓×2 _{0.75} ^{×2}					1.98
O8			0.40		↓×2 _{0.48} ^{×2}				0.70					2.06
O9		↓×2 _{0.28} ^{×2}			0.53					↓×3 _{1.02}				2.11
O10			0.20 ^{×3}								1.13			1.73
O11	0.30	0.15		0.24							↓×3 _{1.19}			1.88
OF12 ^{0.42(O)} ^{0.58(F)}				↓×2 _{0.25} ^{×2}	0.45							↓×2 _{0.41}	↓×3 _{0.09}	1.45
F13	0.24 ^{×3}													0.07
F14		↓×2 _{0.18}	↓×2 _{0.25}	↓×2 _{0.25}	↓×2 _{0.25}									0.93
(W)			0.04 ^{×3}											0.12
	2.60	2.54	2.12	2.02	3.82	2.88	3.96	3.99	2.97	3.06	4.70	1.23	0.58	

Notes: The valence of each site takes account of the contribution of the different atomic species present inside the site or its incomplete occupancy

TABLE 7. Comparison of the possible site population and unit formula of okanoganite and vicanite-(Ce)

	M1	M2	M3	M4	M5	Fe	Si1	Si2	B1	B2	As1	As2	Na	W
Okanoganite	REE	REE	Y	Na, Ca	Y	Fe, Ti	Si	Si	B	B	Si	—	Na	—
Vicanite-(Ce)	Ce, Ca	La, Ca	Ca	Ca	Th, Ca	Fe	Si	Si	B	B	As ⁵⁺ , P	As ³⁺ _{0.4}	Na _{0.6}	(H ₂ O) _{0.2}
Okanoganite	(Na, Ca, REE, Y) ₁₅ Fe ³⁺ (SiO ₄) ₃ (Si ₃ B ₃ O ₁₈)(BO ₃)(SiO ₄)(NaF ₃)F ₁₃ · <i>n</i> H ₂ O													
Vicanite-(Ce)	(Ca, REE, Th) ₁₅ Fe ³⁺ (SiO ₄) ₃ (Si ₃ B ₃ O ₁₈)(BO ₃)(As ⁵⁺ O ₄)(As ³⁺ O ₃) _x (NaF ₃) _{1-x} F ₇ ·0.2H ₂ O with $x = 0.4$													

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