

Proshchenkoite-(Y) from Russia – a new mineral species in the vicanite group: descriptive data and crystal structure

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ABSTRACT

A REE-bearing fluorosilicate from the Tommot REE-Nb deposit in Yakutia, Russia, described without a name in 1966, is characterized here as a new species, proshchenkoite-(Y), of the vicanite group of borosilicates. Wavelength-dispersive electron probe analyses gave the following empirical formula: $(Y_{3.70}REE_{7.54}Ca_{1.55}Na_{1.16}Mn_{0.77}Th_{0.10}Pb_{0.01})_{\Sigma 14.83}(Fe_{0.83}Mn_{0.15}Ti_{0.02})_{\Sigma 1.00}Ca_{1.00}(P_{0.70}Si_{0.26}As_{0.04})_{\Sigma 1.00}Si_{6.05}B_{3.20}(O_{34.55}F_{13.45})_{\Sigma 48}$. Boron was analysed with a nuclear microprobe method based on the nuclear reaction $^{11}B(p,\alpha)2\alpha$. The simplified formula is $(Y,REE,Ca,Na,Mn)_{15}(Fe^{2+},Mn)Ca(P,Si)Si_6B_3O_{34}F_{14}$. The mineral is trigonal, $R3m$, with $a = 10.7527(7)$ Å, $c = 27.4002(18)$ Å, $V = 2743.6(6)$ Å³, $Z = 3$. The crystal structure was refined to $R1 = 0.042$ for 1819 observed reflections. Proshchenkoite-(Y) is isostructural with okanoganite-(Y), vicanite-(Ce) and hundholmenite-(Y), and the differences in site occupancies are discussed. The strongest six reflections of the X-ray powder-diffraction pattern [d_{obs} in Å, (h), (kl)] are: 4.441, (36), (202); 3.144, (77), (214); 3.028, (45), (009); 2.968, (100), (027); 1.782, (32), (330); and 1.713, (32), (1,2,14). The mineral is optically uniaxial (–) with ω 1.734(2) and ϵ 1.728(2). The Mohs hardness is about 5; density measured on material subject to incipient metamictization is 4.72 g/cm³, as compared to $D_{calc} = 4.955$ g/cm³.

The result of electron microprobe analyses of alleged okanoganite-(Y) from the type locality in Okanogan County, Washington, USA, is also presented. We find here also that $P > Si$ at one of the sites, whereas the analytical data of Boiocchi *et al.* (2004) indicate $Si > P$. Consequently, the mineral we have analysed is the P analogue of okanoganite-(Y), another new species.

KEYWORDS: proshchenkoite-(Y), new mineral species, okanoganite-(Y), vicanite group, REE borosilicate, electron-microprobe data, nuclear microprobe data, crystal structure, Tommot REE-Nb deposit, Russia.

Introduction

THE vicanite group of Strunz and Nickel (2001) up to now includes three borosilicate mineral species: okanoganite-(Y) (Boggs, 1980; Boiocchi

et al., 2004), vicanite-(Ce) (Maras *et al.*, 1995; Ballirano *et al.*, 2002) and hundholmenite-(Y) (Raade *et al.*, 2007). The minerals are trigonal, $R3m$, with similar, layered structures. The silicate layer contains an octahedron with Al, Fe³⁺ and Ti as the central atoms, sharing corners with six SiO₄ tetrahedra in a pinwheel fashion. BO₄ tetrahedra form threefold rings with each tetrahedron sharing a corner with one SiO₄ tetrahedron, resulting in an (Si₃B₃O₁₈)^{15–} polyanion (Ballirano *et al.*, 2002, Boiocchi *et al.*, 2004; Raade *et al.*, 2007). A

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single tetrahedral site contains variable amounts of As, P and Si. Vicanite-(Ce) is peculiar in having an additional three-coordinated boron atom (Ballirano *et al.*, 2002).

In 1966, an unnamed fluorosilicate of REEs was described from a Siberian pegmatite (Proshchenko *et al.*, 1966). Its cell dimensions and X-ray powder diffraction pattern are quite similar to those of okanoganite-(Y), as was recognized by Boggs (1980). Semenov (2001) also treated the Siberian mineral as closely related to okanoganite-(Y), although boron was not found in the wet chemical analysis reported by Proshchenko *et al.* (1966). We have had access to the Siberian mineral in the form of separated grains, prepared by the Russian authors, and are able to prove the boron content of the mineral. It is well known that in a wet chemical analysis, boron may be mistaken for aluminium. The analysis of Proshchenko *et al.* (1966) gave 1.27 wt.% Al₂O₃, whereas Al is below the detection limit in our electron microprobe (EMP) analyses (see below). The objective of this paper is to describe the mineral as the new species proshchenkoite-(Y), based on a complete chemical analysis and a crystal structure determination, and to make a comparison with new analytical data of okanoganite-(Y) from the type locality (Okanogan County, Washington, USA).

Proshchenkoite-(Y) is named for Evgeniy Grigor'evich Proshchenko (Евгений Григорьевич Проценко) (1929–1996), Russian mineralogist and senior author of the paper on the unnamed REE fluorosilicate from Siberia. The mineral and name were approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) (IMA No. 2007–007). Type material is held in the mineral collection of the Natural History Museum, University of Oslo, with catalogue number 42029.

Occurrence and mineral parageneses

The unnamed REE fluorosilicate of Proshchenko *et al.* (1966) was stated to be found in 'one of the pegmatite fields of Siberia'. According to Igor V. Pekov (pers. comm. 2008), the locality is undoubtedly the Tommot REE-Nb deposit in Yakutia, Russia. Also, Semenov (2001) has identified the locality as Tommot. The information given below is taken from the 1966 Russian paper.

Lower Palaeozoic crystalline schists and gneisses of the area are located in the cores of

anticlinal folds. With the latter is associated a differentiated gabbroic massif of concentrically zoned structure, in the exocontact zone of which are developed syenites, fenitized granite gneisses and pegmatites of syenitic to alkali granitic composition. The enclosing crystalline schists are in places syenitized, and the granite gneisses and pegmatites in individual areas have undergone intense aegirization and albitization.

Proshchenkoite-(Y) occurs rather often in the pegmatites and also in the enclosing crystalline schists and aegirized gneisses. In most cases it forms nest-like accumulations of irregular form, thin veinlets or small disseminations. Thin, monomineralic veinlets of the mineral cut the aegirized gneisses with distinct contacts, and the description of the mineral is based on a sample selected from such veinlets. According to Proshchenko *et al.* (1966), "the geological conditions of occurrence and character of the mineral associations confirm its pneumatolytic-hydrothermal nature".

Associated minerals include chevkinite, fergusonite, gadolinite, britholite, alkali amphibole, fluorite, pyrite and molybdenite. Levinson suffixes for the REE minerals are not specified by Proshchenko *et al.* (1966). An unnamed hydrated yttrium calcium carbonate was described from the Tommot deposit by Nekrasov *et al.* (1992); it is undoubtedly identical with kamphaugite-(Y). The carbonate is associated with chevkinite-monzonite-britholite ores which also contain yttrialite, gadolinite and zircon.

Physical data

The Proshchenko *et al.* (1966) paper does not mention any sizes of aggregates or individual mineral grains. The irregular grains of the mineral concentrate measure up to 0.3 mm. The properties recorded below are extracted from the Russian paper.

The colour is brownish to reddish, orange-yellow in thin fragments, and the streak is light brown. The mineral is translucent to transparent and has a vitreous to greasy lustre. The fracture is uneven, in places conchoidal. It is non-fluorescent. Mohs hardness is 5; the mineral is brittle and shows no cleavage. A density of 4.72 g/cm³ was obtained by direct measurement of volume and weight on a micro-sample. Owing to incipient metamictization, the measured density is distinctly lower than the one calculated using single-crystal data, 4.955 g/cm³.

The mineral is optically uniaxial negative with ω 1.734(2) and ε 1.728(2) (presumably measured in white light). The indices of refraction are variable because of partial metamictization, involving hydration. Such hydrated products have lower indices of refraction: $\omega \sim 1.702$, $\varepsilon \sim 1.698$.

A Differential Thermal Analysis (DTA) study featured a single, distinct endothermal effect in the interval 910–990°C, with a maximum at 970°C, accompanied by a loss of weight of about 5% (probably partial loss of fluorine and water of metamictization).

Chemical data

Analytical details

Wavelength-dispersive analyses were performed with a Cameca SX100 electron probe at 20 kV operating voltage and 20 nA probe current, with 10 s counting time on both peak and background (20 s for P-K β) and a beam diameter of 10 μ m. The probe standards and peaks measured were: omphacite (Na-K α), wollastonite (Ca-K α and Si-K α), pyrophanite (Mn-K α and Ti-K α), galena (Pb-M α), Al₂O₃ (Al-K α), Fe₂O₃ (Fe-K α), REEPO₄ (L α lines for Y, La, Ce, Tb and Yb; L β lines for Pr, Nd, Eu, Gd, Dy, Ho, Er, Tm and Lu), a synthetic oxide containing Y, Tb and Sm (measured on the L β line), a synthetic glass containing 14.97 wt.% ThO₂ (Th-M α), GaAs (As-L α), synthetic fluorophlogopite (F-K α) and a Durango apatite (P-K β). Phosphorus was measured on the K β line to avoid interference with Y-L β on the TAP analysing crystal. The REEPO₄ standards are described by Jarosewich and Boatner (1991). It was suspected that the Fe content in the analyses was too low, as was the case for hundholmenite-(Y) (Raade *et al.*, 2007). The explanation was found to be a background interference from the Dy-L α peak. Consequently, Fe was redetermined by applying a trace element procedure provided by Cameca in the EMP software. The elemental composition, as initially determined, but omitting the Fe value, was entered into the procedure which then calculated the matrix correction factors for the given analysis. Using these factors, Fe was then re-analysed at 20 kV, 20 nA and 20 s counting time on peak and background using more suitable positions for the background measurement. This procedure is only valid for elements with concentrations ~ 3 wt.%. The corrected concentrations are shown in Table 1.

Boron was determined by a nuclear microprobe method, based on the nuclear reaction $^{11}\text{B}(p,\alpha)^8\text{Be}$ described by Skogby *et al.* (2003), who showed that the method was virtually matrix insensitive for the light-element minerals in their study. However, a heavy-element correction had to be employed for REE-bearing proshchenkoite-(Y). Even so, the results were not quite satisfactory, due to the large matrix difference between the sample and the tourmaline standard (from Varuträsk, Sweden). It was therefore decided to use the boron content in hundholmenite-(Y), determined by ICP-AES and corrected for a 3% contamination with yttrian fluorite to 3.92 wt.% B₂O₃ (Raade *et al.*, 2007), as a standard in the nuclear microprobe analysis. This procedure gave boron contents in good agreement with the stoichiometric demands of vicanite-group minerals.

Owing to a dearth of material, samples were not analysed for water. The wet chemical analysis of the Russian mineral (Table 1, analysis 2) shows 2.00 wt.% H₂O (Proshchenko *et al.*, 1966). Backscattered electron (BSE) images of five analysed grains indicated areas of alteration, probably incipient metamictization, which may explain some of the water content in the sample. Such areas were avoided in the analyses in this study, and the mean analytical sum is close to 100 wt.% (Table 1). For okanoganite-(Y) from the type locality with 1.33 wt.% H₂O, the presence of OH is indicated by the structural study (Boiocchi *et al.*, 2004). The low sum in the mean analytical result (97.57 wt.%) may also indicate the presence of some water. However, Boggs (1980) did not detect any significant amount of hydrogen in okanoganite-(Y) by an ion microprobe scan.

Analytical results

The mean results of the EMP analyses of proshchenkoite-(Y) and of type locality okanoganite-(Y) are presented in Table 1, where the analytical results of Proshchenko *et al.* (1966) and Boiocchi *et al.* (2004) are also included for comparison.

The empirical formula of proshchenkoite-(Y), on the basis on (O+F) = 48, is:

$$(\text{Y}_{3.70}\text{REE}_{7.54}\text{Ca}_{1.55}\text{Na}_{1.16}\text{Mn}_{0.77}\text{Th}_{0.10}\text{Pb}_{0.01})_{\Sigma 14.83}(\text{Fe}_{0.83}^{2+}\text{Mn}_{0.15}\text{Ti}_{0.02})_{\Sigma 1.00}\text{Ca}_{1.00}(\text{P}_{0.70}\text{Si}_{0.26}\text{As}_{0.04})_{\Sigma 1.00}\text{Si}_{6.05}\text{B}_{3.20}(\text{O}_{34.55}\text{F}_{13.45})_{\Sigma 48}$$

Iron is regarded as divalent, in accordance with the structure refinement (see below). The composition of the individual REEs is:

TABLE 1. Chemical analyses (wt.%) of proshchenkoite-(Y) from Russia and okanoganite-(Y) from the type locality in the USA.

	— Russia —		— USA —	
	1	2	3	4
Li ₂ O	n.a.	n.a.	n.a.	0.02
Na ₂ O	1.32	2.11	1.61	1.87
BeO	n.a.	n.a.	n.a.	<0.01
MgO	n.d.	0.20	n.d.	n.d.
CaO	5.23	5.60	4.82	5.50
MnO	2.38	2.15	0.15	n.a.
SrO	n.a.	n.a.	n.a.	0.08
BaO	n.a.	n.a.	n.a.	0.08
PbO	0.12	n.a.	1.00	0.01*
B ₂ O ₃	4.08	n.d.	3.76	3.80
Al ₂ O ₃	n.d.	1.27	0.38	n.a.
Fe ₂ O ₃		3.69	1.78	2.18
FeO**	2.19**			
Y ₂ O ₃	15.30	14.01	17.85	18.94
La ₂ O ₃	5.54	6.25	4.23	7.60
Ce ₂ O ₃	15.24	13.71	11.81	14.37
Pr ₂ O ₃	1.95	2.37	1.81	1.88
Nd ₂ O ₃	9.79	9.22	8.62	7.52
Sm ₂ O ₃	2.78	3.03	2.98	2.07
Eu ₂ O ₃	0.89	n.a.	0.79	0.01
Gd ₂ O ₃	3.93	4.19	4.79	2.69
Tb ₂ O ₃	0.36	0.42	0.48	0.48
Dy ₂ O ₃	3.02	3.52	3.98	3.23
Ho ₂ O ₃	0.47	0.85	0.66	n.a.
Er ₂ O ₃	1.54	1.70	1.81	1.88
Tm ₂ O ₃	0.38	0.06	0.42	0.20
Yb ₂ O ₃	0.91	1.34	0.51	0.87
Lu ₂ O ₃	0.26	n.a.	0.19	n.a.
SiO ₂	13.90	14.0	12.98	14.94
TiO ₂	0.07	0.14	1.07	0.56
ThO ₂	0.93	0.93	1.47	1.87
UO ₂	n.d.	n.a.	n.d.	0.08
P ₂ O ₅	1.83	2.83	2.13	0.83
As ₂ O ₅	0.18	n.a.	0.52	n.a.
H ₂ O	n.a.	2.00	n.a.	1.33
F	9.36	7.85	8.59	7.07
Sum	103.95	103.44	101.19	101.96
—O≡F ₂	3.94	3.31	3.62	2.98
Total	100.01	100.13	97.57	98.98

1 – This work. Mean of ten EMP analyses on five grains (for FeO, 15 analyses on five grains). B₂O₃ was determined by nuclear microprobe analysis on one grain.

2 – Proshchenko *et al.* (1966). Wet chemical analysis (individual REEs by paper chromatography from the total REEs separated chemically).

3 – This work. Mean of nine EMP analyses on a single grain (for Fe₂O₃, four analyses). B₂O₃ was determined by nuclear microprobe analysis.

4 – Boiocchi *et al.* (2004). EMP analysis of Na, Ca, Fe, Ti, Si and P; secondary ion mass spectrometry (SIMS) for the other elements.

* Given as PbO₂

** According to the structure refinement, Fe is mainly divalent in proshchenkoite-(Y).

n.a. – not analysed

n.d. – not detected

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(La_{0.93}Ce_{2.53}Pr_{0.32}Nd_{1.59}Sm_{0.44}Eu_{0.14}Gd_{0.59}Tb_{0.05}Dy_{0.44}Ho_{0.07}Er_{0.22}Tm_{0.05}Yb_{0.13}Lu_{0.04})_{Σ7.54}, which corresponds to a mean atomic number of 60.4, i.e. close to Nd. The Gladstone-Dale relationship gives a compatibility index $1 - (K_P/K_C) = 0.030$ using calculated density and single-crystal cell volume and = -0.019 using measured density and single-crystal cell volume; these indices are rated as 'excellent' and 'superior', respectively (Mandarino, 1981).

The mean analytical result for alleged okanoganite-(Y) from the type locality gives the following empirical formula, on the basis of (O+F) = 48:

(Y_{4.41}REE_{6.99}Ca_{2.40}Na_{0.45}Fe_{0.20}Th_{0.16}Pb_{0.13}Mn_{0.06})_{Σ14.80}(Fe³⁺_{0.42}Ti_{0.37}Al_{0.21})_{Σ1.00}Na_{1.00}(P_{0.84}As_{0.13}Si_{0.03})_{Σ1.00}Si_{6.00}B_{3.01}(O_{35.39}F_{12.61})_{Σ48}. Here, octahedrally coordinated Fe is considered to be trivalent, in agreement with the structure data for okanoganite-(Y) (Boiocchi *et al.*, 2004). A surplus of Fe is included with Y, REE, etc. but without valence indication, as it might well be divalent in this case. Since P > Si at the single tetrahedral site, the mineral is most likely the P analogue of okanoganite-(Y), another new species.

Both empirical formulae are in good agreement with the general formula of okanoganite-related minerals: $[^{8-10}]Y, REE, Ca, Na, Mn, Th)_{15} [^{6}]Fe, Al, Ti [^{10}]Na, Ca [^{4}]Si, P, As) Si_6 B_3 (O, F)_{48}$. The ten-coordinated site that can host both Na and Ca contains, according to our structure refinement, only Ca in the case of proshchenkoite-(Y)

but most likely Na in the case of the P analogue of okanoganite-(Y), as was found by Boiocchi *et al.* (2004).

REE patterns

Chondrite-normalized REE patterns, shown in Fig. 1 (CI normalization values from McDonough and Sun, 1995), are generally smooth with a slight relative enrichment in LREEs. The analytical results show a good agreement with the previously published data, especially for LREEs; larger variations in HREEs can mainly be ascribed to analytical inaccuracies, notably for HREEs with the lowest concentrations (e.g. Tm). However, there is a remarkable difference in Eu values. A large negative Eu anomaly, like the one described by Boiocchi *et al.* (2004), is not present in these data sets; the Eu results plot in line with the main trend of the REE patterns, as is the case for the related mineral hundholmenite-(Y) (Raade *et al.*, 2007).

X-ray diffraction (XRD)

Powder XRD

The powder XRD pattern was recorded with a Philips X'Pert diffractometer using Cu-K α radiation (Table 2). The refined cell parameters are $a = 10.712(8)$ Å, $c = 27.35(3)$ Å. Owing to partial metamictization, the reflections are not as well resolved as for the other vicanite-group minerals. For instance, the strongest ($I = 100$) proshchen-

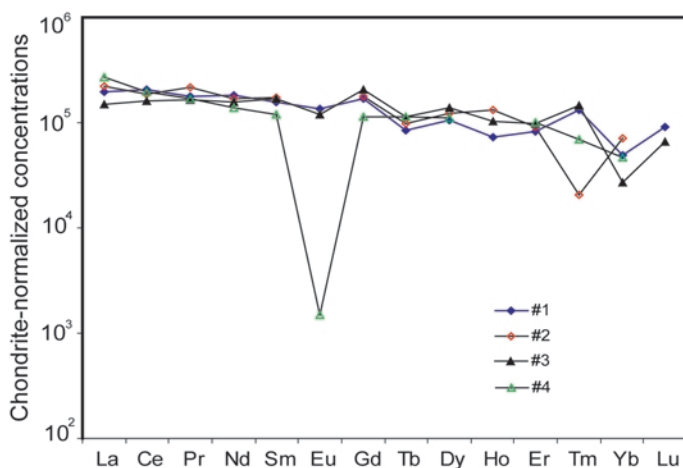


FIG. 1. Chondrite-normalized REE patterns for proshchenkoite-(Y) and okanoganite-(Y) (analyses 1 to 4 in Table 1). Normalization to CI chondrite values, taken from McDonough and Sun (1995).

TABLE 2. Powder XRD data for proshchenkoite-(Y).

hkl_0	d_{obs} (Å)	d_{calc} (Å)	$h k l$
28	4.774	4.711	0 1 5
18	4.575	4.573	0 2 1
36	4.441	4.393	2 0 2
10	3.641	3.600	1 0 7
77 b	3.144	3.120	2 1 4
45 b	3.028	3.038	0 0 9
100 b	2.968	2.988	0 2 7
30	2.672	2.678	2 2 0
8	2.512	2.528	3 1 2
8	2.392	2.401	0 1 11
5	2.211*	2.196	4 0 4
15	2.172	2.167	3 0 9
17	2.141	2.135	0 4 5
18 b	2.029	2.032	3 2 4
20 b	1.993	1.994	4 0 7
20 b	1.986	1.983	2 3 5
12	1.923	1.916	0 2 13
12	1.874	1.874	1 3 10
		1.869	3 2 7
30	1.806	1.807	2 3 8
32	1.782	1.785	3 3 0
32	1.713	1.706	1 2 14
5	1.652*	1.654	1 5 2
10	1.615	1.619	5 1 4
		1.617	2 3 11
6	1.513	1.516	3 4 2
7	1.414	1.413	1 6 1
		1.412	5 2 6
12	1.386	1.385	1 6 4
		1.384	1 5 11
12	1.372	1.376	4 0 16
		1.375	0 2 19

Cu-K α radiation.

b = broad reflection.

Refined cell parameters: $a = 10.712(8)$ Å, $c = 27.35(3)$ Å.

* not used for calculation of cell parameters.

koite-(Y) reflection, (027) at $d = 2.968$ Å, corresponds to three strong reflections in the hundholmenite-(Y) pattern with indices (027), (125) and (303) and intensities 100, 76 and 66, respectively (Raade *et al.*, 2007).

Single-crystal XRD

The single crystal of proshchenkoite-(Y) was a transparent, orange-yellow fragment measuring $60 \mu\text{m} \times 100 \mu\text{m} \times 120 \mu\text{m}$. Intensity data were

rather weak due to the small crystal size and the metamict nature of this mineral. Intensity data were collected on a fully automated Bruker *P4* four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated Mo-K α radiation and a 4K APEX CCD detector mounted at 6 cm distance from the crystal. Integrated intensities were collected up to $\theta = 30^\circ$, using 30 s frame counts and a frame width of 0.25° . Intensity of spots falls off dramatically after $\theta = 25^\circ$. Refinement of the structure without data beyond $\theta = 25^\circ$ improved the R index a little ($R = 0.031$) but increased the standard deviations of the atomic parameters and subsequently those of the bond lengths. Data pertinent to the intensity data collection are given in Table 3. The unit-cell parameters for the single crystal were refined using 5862 indexed reflections with $I > 10\sigma(I)$.

Reduction of the intensity data, structure determination and structure refinement were done with the *SHELXTL* (Sheldrick, 1990) package of computer programs. Data reduction included corrections for background, scaling and Lorentz-polarization factors. An empirical absorption correction (*SADABS*, Sheldrick, 1998) was applied. In the data reduction, there was some indication that the symmetry should be lowered to monoclinic space group *Im* (a non-standard setting of space group *Cm*). However, the authors could not rationalize this symmetry reduction as there was no apparent ordering nor any structural changes that would justify lowering the symmetry. Consequently, *R3m* space group (SG 160) was used, and the starting atom coordinates were those determined for hundholmenite-(Y) (Raade *et al.*, 2007). In the last stage of refinement, there were electron residuals of $+2.33$ and $-1.20 \text{ e}/\text{Å}^3$. In the final least-squares refinement, all atoms were refined with anisotropic displacement factors. The weighting scheme is inversely proportional to $\sigma^2(F)$. The addition of an isotropic extinction correction did not improve the refinement. However, including the inversion centre twin did improve the refinement slightly.

Crystal data, data collection information and refinement details are given in Table 3. The final atomic coordinates and displacement parameters are shown in Table 4; bond distances and selected angles are presented in Table 5. A table of structure factors is deposited with the Principal Editor of *Mineralogical Magazine* and are available at: http://www.minersoc.org/pages/e_journals/dep_mat_mm.html

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TABLE 3. Crystal data, data-collection information and refinement details for proshchenkoite-(Y).

Space group	<i>R3m</i>	Measured reflections (Ewald sphere)	5785
<i>a</i> (Å)	10.7527(7)	Unique reflections (Friedels not merged)	2056
<i>c</i> (Å)	27.4002(18)	Observed reflections [$> 4\sigma(F)$]	1819
<i>V</i> (Å ³)	2743.6(6)	Merged Friedel reflections	1041
<i>Z</i>	3	<i>R</i> (int)	0.039
		Goodness of fit on F^2	1.10
μ (mm ⁻¹)	20.0	<i>R1/wR2</i> all unique data	0.049/0.102
Crystal size (µm)	60 × 100 × 120	<i>R1</i> for observed, unique data	0.042
θ range for data	30°	<i>R1</i> for Friedel merged data	0.039
Ideal unit-cell contents	3[(Y,REE) ₁₅ (Fe,Mn)Ca(P,Si)Si ₆ B ₃ O ₃₄ F ₁₄]		

Crystal structure

In the refinement, the occupancies of the Fe/Mn and P/Si sites were fixed according to the result of the chemical analysis. Table 6 shows refined site occupancy factors for the *M1–M5* and *Ca* sites, the latter being fully occupied by Ca. The distribution of Y, REE, Na, Ca and Mn among the five *M* sites is a problematic issue. We have used Nd as being close to a weighted average of the REEs (exclusive of Y) but we do not know if the REEs are distributed in the same ratio at all five sites. The question of a correct assignment of five components (plus minor amounts of Th and Pb) at the *M* sites is practically impossible to solve. Accordingly, the site populations presented in Table 6 are only tentative. We have allocated Na, Mn and a significant amount of Ca to the sites with low electron densities (*M3* and *M4*). It is reasonable to assume that Y and Mn are concentrated in polyhedra with the lowest mean bond distances, *M4* and *M5* (Table 5). Thorium is placed at *M5* in accordance with the situation in vicanite-(Ce) (Ballirano *et al.*, 2002). The sum of the refined site scattering for *M1* to *M5*, 656.1 e.p.f.u., compares reasonably well with the total number of electrons calculated from the empirical formula, 669.5 e.p.f.u., the difference amounting to 2% relative to the mean value.

Although the *M3* site was refined with Y and Ca (refinement with Na and Ca failed), the assigned site population includes Na and Nd as well (Table 6). The mean number of electrons associated with 1.16 Na + 1.00 Nd is 33.7 [(1.16 × 11 + 1.00 × 60)/2.16 = 33.7] as compared to 25.2 electrons for 0.61Ca + 0.23Y, which shows that no large error is introduced. Similarly, the mean number of electrons asso-

ciated with Ca + Mn + Nd at *M4* is 42.8, which compares well with refinement on Y (atomic number 39).

A bond valence table was presented for hundholmenite-(Y) (Raade *et al.*, 2007). It gave satisfactory bond valence sums for all cations except for three of the *M* sites. It was further shown that the sum of the site charges for *M1* to *M5* compared well with the bond valence sums for these sites. Owing to the uncertainty in cation distributions among *M1–M5*, this exercise is not repeated for proshchenkoite-(Y).

An important difference from the other vicanite-group minerals is the significantly longer mean Fe–O distance of 2.132 Å in proshchenkoite-(Y) (Table 5) [$\langle \text{Fe}/\text{Al}-\text{O} \rangle$ is 2.016 Å for vicanite-(Ce), 2.011 Å for okanoganite-(Y) and 1.966 Å for hundholmenite-(Y)]. Bond valence calculations with parameters from Brese and O’Keeffe (1991) indicate that Fe in proshchenkoite-(Y) must be predominantly divalent instead of trivalent (calculation with all Fe as Fe²⁺ gives 2.05 v.u., as opposed to 2.19 v.u. for Fe³⁺ and 2.38 v.u. for Mn²⁺). The actual empirical composition at the octahedral site, (Fe_{0.83}²⁺Mn_{0.15}Ti_{0.02})_{Σ1.00}, gives a bond valence sum of 2.11 v.u. (the total number of electrons at the site is 2.04).

The empirical formula apparently indicates a surplus of boron amounting to 0.20 B a.p.f.u., corresponding to no more than 1.0 e.p.f.u. Is this real or just the effect of analytical inaccuracy? It should be noted that the present okanoganite-(Y) sample, analysed by the same method, has 3.01 B in the empirical formula, very close to the stoichiometric requirement. Three-coordinated B in vicanite-(Ce) has coordinates 0,0,0.1467(6) and bond distance B2–O9 (× 3) 1.365(4) Å

TABLE 4. Fractional coordinates and displacement parameters (\AA^2) for proshchenkoite-(Y). M = site multiplicity.

Site	M	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M1	9	0.87001(3)	0.12999(3)	0.68367(3)	0.01697(15)	0.01697(15)	0.0179(3)	-0.00201(10)	0.00201(10)	0.00637(18)	0.01824(14)
M2	9	0.86573(3)	0.13427(3)	0.10116(3)	0.02088(17)	0.02088(17)	0.0228(3)	0.00088(12)	-0.00088(12)	0.0096(2)	0.02187(16)
M3	9	0.11449(8)	0.8851(8)	-0.09902(7)	0.0263(4)	0.0263(4)	0.0480(9)	-0.0101(3)	0.0101(3)	0.0147(5)	0.0328(4)
M4	9	0.12282(6)	0.87718(6)	0.46990(4)	0.0183(3)	0.0183(3)	0.0201(5)	-0.0019(2)	0.0019(2)	0.0043(3)	0.0211(3)
M5	9	0.13824(4)	0.86176(4)	0.22186(4)	0.01782(18)	0.01782(18)	0.0170(3)	0.00037(13)	-0.00037(13)	0.0104(2)	0.01688(17)
Fe/Mn	3	0	0	0	0.0253(8)	0.0253(8)	0.0139(10)	0	0	0.0127(4)	0.0215(5)
Si1	9	0.16972(16)	0.83028(16)	0.04725(11)	0.0182(6)	0.0182(6)	0.0255(13)	-0.0004(6)	0.0004(6)	0.0068(9)	0.0217(6)
Si2	9	0.82858(16)	0.17142(16)	-0.04047(10)	0.0167(6)	0.0167(6)	0.0255(13)	0.0006(5)	-0.0006(5)	0.0086(8)	0.0195(6)
Bi	9	-0.0821(6)	0.0821(6)	0.2962(4)	0.010(2)	0.010(2)	0.025(5)	0.005(2)	-0.005(2)	-0.004(3)	0.019(2)
P/Si	3	0	0	0.78864(19)	0.0325(14)	0.0325(14)	0.027(2)	0	0	0.0163(7)	0.0308(10)
Ca	3	0	0	0.57832(16)	0.0398(14)	0.0398(14)	0.0211(17)	0	0	0.0199(7)	0.0336(11)
O1	9	0.0837(4)	-0.0837(4)	0.0525(3)	0.0147(17)	0.0147(17)	0.041(4)	0.0042(16)	-0.0042(16)	0.003(2)	0.0252(17)
O2	9	0.1867(4)	0.8133(4)	-0.0102(3)	0.0276(19)	0.0276(19)	0.027(4)	-0.0038(16)	0.0038(16)	0.014(2)	0.0272(17)
O3	18	0.3274(5)	-0.0683(5)	0.07292(17)	0.0237(2)	0.025(2)	0.022(2)	0.0048(19)	-0.0003(19)	0.0133(17)	0.0233(11)
O4	9	-0.0852(4)	0.0852(4)	-0.0526(4)	0.0234(19)	0.0234(19)	0.065(6)	-0.002(2)	0.002(2)	0.013(2)	0.037(2)
O5	9	0.8107(4)	0.1893(4)	0.0188(3)	0.0247(18)	0.0247(18)	0.016(3)	0.0009(14)	-0.0009(14)	0.012(2)	0.0218(15)
O6	18	0.6661(6)	0.0851(6)	-0.06171(19)	0.020(2)	0.037(3)	0.025(3)	-0.008(2)	-0.008(2)	0.005(2)	0.0312(13)
O7	9	0.0778(4)	-0.0778(4)	0.3069(3)	0.0202(18)	0.0202(18)	0.031(4)	-0.0024(15)	0.0024(15)	0.007(2)	0.0251(16)
O8	9	-0.0977(4)	0.0977(4)	0.2408(3)	0.0223(19)	0.0223(19)	0.018(3)	-0.0005(15)	0.0005(15)	0.005(3)	0.0235(16)
F9	9	0.0852(4)	-0.0852(4)	0.1475(3)	0.042(2)	0.042(2)	0.035(4)	0.0044(17)	-0.0044(17)	0.015(3)	0.0425(19)
O10	3	0	0	0.8468(5)	0.029(4)	0.029(4)	0.027(7)	0	0	0.015(2)	0.028(3)
O11*	18	0.1514(12)	0.1192(14)	0.7680(4)	0.027(5)	0.055(9)	0.033(6)	0.001(5)	-0.003(5)	-0.005(5)	0.049(5)
F12	9	-0.0899(4)	0.0899(4)	0.5124(3)	0.0287(17)	0.0287(17)	0.038(4)	-0.0074(15)	0.0074(15)	0.011(2)	0.0333(16)
F13	3	0	0	0.6633(4)	0.014(2)	0.014(2)	0.038(5)	0	0	0.0072(12)	0.022(2)
F14	18	0.0156(6)	0.3030(6)	0.84079(19)	0.043(2)	0.050(3)	0.042(3)	-0.005(2)	-0.015(2)	0.026(2)	0.0437(14)
F15	3	0	0	0.4377(5)	0.052(5)	0.052(5)	0.037(7)	0	0	0.026(2)	0.047(3)

* Occupancy of O11 is 0.5

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TABLE 5. Bond distances (Å) and selected bond angles (°) in proshchenkoite-(Y).

M1–F13	2.485(3)	Si1–O2	1.605(8)
–O3 × 2	2.511(5)	–O1	1.608(8)
–O6 × 2	2.536(6)	–O3 × 2	1.646(5)
–O5 × 2	2.562(4)	<Si1–O>	1.626
–O11	2.564(12)		
–O7	2.624(8)	O1–Si1–O2	106.5(4)
<M1–O>	2.543	O1–Si1–O3 × 2	106.2(3)
		O2–Si1–O3 × 2	110.9(2)
M2–O5	2.479(7)	O3–Si1–O3	115.6(4)
–F9 × 2	2.533(4)		
–O1 × 2	2.562(4)	Si2–O6 × 2	1.622(5)
–F14 × 2	2.630(6)	–O4	1.640(9)
–O3 × 2	2.668(6)	–O5	1.657(7)
–O11	2.778(14)	<Si2–O>	1.635
<M2–O>	2.604		
		O4–Si2–O5	113.3(5)
M3–O8	2.264(8)	O4–Si2–O6 × 2	110.8(3)
–O4 × 2	2.302(6)	O5–Si2–O6 × 2	105.3(3)
–F14 × 2	2.309(6)	O6–Si2–O6	111.1(4)
–O10	2.599(7)		
–O2	2.781(8)	B1–O2	1.411(14)
–O6 × 2	3.057(6)	–O7 × 2	1.519(7)
<M3–O>	2.553	–O8	1.545(13)
		<B1–O>	1.499
M4–O3 × 2	2.300(5)		
–F14 × 2	2.354(5)	O2–B1–O7 × 2	110.5(6)
–F12 × 2	2.358(4)	O2–B1–O8	110.8(8)
–F15	2.452(5)	O7–B1–O7	111.3(9)
–O11	2.731(12)	O7–B1–O8 × 2	106.9(6)
<M4–O>	2.401		
		P/Si–O11 × 3	1.590(11)
M5–F9	2.264(7)	–O10	1.592(14)
–F12	2.283(7)	<P/Si–O>	1.591
–O6 × 2	2.318(5)		
–O8 × 2	2.350(2)	O10–P/Si–O11 × 3	110.9(4)
–O7	2.589(7)	O11–P/Si–O11 × 3	108.0(5)
–F14 × 2	2.590(6)		
<M5–O>	2.406	Ca–F13	2.328(12)
		–F12 × 3	2.464(8)
Fe/Mn–O1 × 3	2.121(8)	–O6 × 6	2.764(6)
–O4 × 3	2.143(9)	<Ca–O>	2.630
<Fe/Mn–O>	2.132		
O1–Fe/Mn–O1 × 3	79.1(3)		
O1–Fe/Mn–O4 × 6	100.6(2)		
O4–Fe/Mn–O4 × 3	79.7(4)		

(Ballirano *et al.*, 2002). At a closely situated site, with coordinates 0,0,0.1619, the proshchenkoite-(Y) structure refinement shows a Fourier difference peak with an electron density of 1.22 e/Å³. In this case, the closest neighbour is F9 (× 3) with a distance of 1.63 Å.

In summary, the proshchenkoite-(Y) structure has, like the other members of the vicanite group, three distinct layers parallel to (001) (Raade *et al.*, 2007):

(1) Layer A contains an octahedron which hosts (Fe²⁺, Mn, Ti) as the central atoms, sharing corners

TABLE 6. Site-occupancy factors and tentative site populations in proshchenkoite-(Y).

Site	sfac	sof	ss e.p.f.u. (X-ray)	Site populations assigned*	e.p.f.u. (EMPA)
M1	Nd	0.4476(10)	161.1	2.10 Nd + 0.90 Y	161.1
M2	Nd	0.4330(10)	155.9	2.40 Nd + 0.60 Ca	156.0
M3	Y	0.2754 (18)	91.4	1.16 Na + 1.00 Nd +	93.9
	Ca	0.2247		0.61 Ca + 0.23 Y	
M4	Y	0.4834(19)	113.1	1.25 Nd + 0.77 Mn	119.4
				+ 0.47 Y + 0.34 Ca	
				+ 0.17 □	
M5	Nd	0.1394(9)	134.6	2.10 Y + 0.79 Nd +	139.1
	Y	0.3607		0.10 Th + 0.01 Pb	
Ca	Ca	0.167(2)	20.0	1.00 Ca	20.0

* Corresponding to the number of atoms in the empirical formula (a.p.f.u.) ($Z = 3$): $(Y_{3.70}REE_{7.54}Ca_{1.55}Na_{1.16}Mn_{0.77}Th_{0.10}Pb_{0.01})_{\Sigma 14.83}$. Nd is the weighted average of the REEs.
 sfac: scattering factor
 sof: site occupancy factor
 ss: site scattering
 e.p.f.u.: electrons per formula unit

with six SiO_4 groups in the form of a pinwheel. In the other vicanite-group minerals, this octahedron is predominantly occupied by (Fe^{3+}, Al, Ti) . BO_4 tetrahedra of the same layer form threefold rings, and each BO_4 tetrahedron of the rings shares a corner with one SiO_4 tetrahedron, producing an $(Si_3B_3O_{18})^{15-}$ polyanion.

(2) Layer B contains a single tetrahedron which incorporates variable amounts of (P, Si, As). This tetrahedron occurs in two orientations with the same probability of occurrence (Balliano *et al.*, 2002; Raade *et al.*, 2007). In vicanite-(Ce), a BO_3 triangle is also present in this layer.

(3) Layer C may contain two very close polyhedra of As^{3+} in threefold coordination and (Ca, Na) in tenfold coordination, which are mutually exclusive (Ballirano *et al.*, 2002; Raade *et al.*, 2007). The As^{3+} site is empty in proshchenkoite-(Y) and okanoganite-(Y), and proshchenkoite-(Y) has only ten-coordinated Ca in this layer.

A three-dimensional network of five different polyhedra with coordinations from eight to ten (M1 to M5) contains (Y, REE, Ca, Na, Mn, Th) and provides connections among the three layers.

Discussion

Except for B_2O_3 and Al_2O_3 in the Russian mineral, as discussed above, there is a remarkably

good agreement between our analytical results and the data obtained by wet chemical analysis, in particular the REE data which were obtained by paper chromatography by Proshchenko *et al.* (1966). The Mn content is greater than in any other analysed mineral of the vicanite group. Proshchenko *et al.* (1966) reported total Fe as 3.69 wt.% Fe_2O_3 ; in another sample, Fe was determined as $FeO = 1.34$ and $Fe_2O_3 = 2.64$ wt.%. It is likely that Fe was oxidized during the metamictization process. However, the considerably smaller amount of total Fe as FeO in our analysis (2.19 wt.%) is not easily explained.

The differences in analytical data between the two okanoganite-(Y) samples from the type locality are not surprising, considering that they were extracted from different miarolitic cavities. The crystal structure refinement of Boiocchi *et al.* (2004) seems to indicate $P > Si$ at the single tetrahedral site, but the estimated error is large, as could be expected for elements that are neighbours in the Periodic System. Their chemical data definitely imply $Si > P$, and in the hundholmenite-(Y) paper (Raade *et al.*, 2007, Table 8), okanoganite-(Y) is defined with $Si > P$. The analytical results presented here indicate $P > Si$ for our sample from Washington Pass. A mineral with $P > Si$ at this particular site is, strictly speaking, a different species from one with $Si > P$, and should be regarded as the P analogue of

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TABLE 7. Comparison of the occupancy at key atom sites for minerals of the vicanite group.

Key atom sites*	Proshchenkoite-(Y) [†]	Hundholmenite-(Y)	Okanoganite-(Y)	Vicanite-(Ce)
<i>M1</i>	0.70 Nd + 0.30 Y	0.64 Sm + 0.36 Y	0.72 Ce + 0.28 Y	0.75 Ce + 0.25 Ca
<i>M2</i>	0.80 Nd + 0.20 Ca	0.75 Sm + 0.25 Ca	0.75 Ce + 0.25 Y	0.74 La + 0.26 Ca
<i>M3</i>	0.39 Na + 0.33 Nd + 0.20 Ca + 0.08 Y	0.44 Ca + 0.28 Sm + 0.10 Y + 0.09 Na + 0.01 Mn + 0.08 □	0.59 Ca + 0.41 Y	0.99 Ca + 0.01 Ce
<i>M4</i>	0.42 Nd + 0.26 Mn + 0.16 Y + 0.11 Ca + 0.05 □	0.56 Y + 0.34 Sm + 0.10 Ca	0.71 Y + 0.29 Ca	0.98 Ca + 0.02 Ce
<i>M5</i>	0.70 Y + 0.26 Nd + 0.033 Th + 0.003 Pb	0.56 Sm + 0.44 Y	0.87 Y + 0.13 Th	0.82 Th + 0.18 Ca
Al/Fe	Fe ²⁺	(Al,Fe ³⁺)	(Fe ³⁺ ,Ti)	Fe ³⁺
[³]B2	empty	empty	empty	B
Si3/As1	(P,Si)	(Si,As ⁵⁺)	(Si,P)	(As ⁵⁺ ,P)
As2**	empty	As ³⁺ < 0.5	empty	As ³⁺ < 0.5
Ca/Na**	Ca	Ca > 0.5	Na	Na > 0.5
O9	F	OH	OH	O
OF12	F	0.64 F + 0.36 O	F	0.58 F + 0.42 O
<i>W</i>	F	0.80 F	OH	0.21 H ₂ O

* Site labelling from the hundholmenite-(Y) paper (Raade *et al.*, 2007).

** The sites As2 and Ca/Na are mutually exclusive.

[†] To facilitate comparison with the other minerals, the atomic contents of the *M1–M5* sites (all with site multiplicity 9) are divided by 3 compared to the figures in Table 6.

okanoganite-(Y). Unfortunately, the crystal used for the microprobe analysis was the only one available to us.

A comparison of the occupancies at key atom sites in the four vicanite-group minerals is given in Table 7. Compared to the other three minerals, proshchenkoite-(Y) has Fe²⁺ at the octahedral site, P predominates at the single tetrahedral site and the Ca/Na site is filled with Ca. There are also differences in the anion positions; the sites previously labelled O9, OF12 and *W* (renamed F9, F12 and F15 in Table 4) contain only F in proshchenkoite-(Y). The five sites filled with F (Table 4) amount to 14 F a.p.f.u., in nice agreement with 13.45 F in the empirical formula.

An important result of the structure refinement, indicating that divalent as well as trivalent elements may enter the octahedral site, implies an even larger number of potential species in the vicanite group. Since a correct distribution of elements at the five *M* sites is not easily made on the basis of site scattering values, it was suggested by Raade *et al.* (2007) that the *M1–M5* polyhedra should be treated as an entity with regard to nomenclature.

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