THE CRYSTAL CHEMISTRY OF SCHCHERBAKOVITE
FROM THE KHIBINA MASSIF, KOLA PENINSULA, RUSSIA

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ABSTRACT

The crystal structure of shcherbakovite from Mount Rasvumchott, Khibina massif, Kola Peninsula, Russia, ideally K2 Na Ti4+2 O (OH) [Si4O12], a 8.1538(4), b 10.5569(5), c 13.9882(6) Å, V 1204.1(2) Å3, space group Imma, Z = 4, Dcalc 3.194 g/cm3, has been refined to R1 = 3.2% for 960 unique (F0 > 4σ(F)) reflections collected on a Bruker single-crystal P4 diffractometer equipped with a CCD detector and MoKa X-radiation. Schcherbakovite occurs in late (hydrothermal) shallowly dipping veins of natrolite and is associated with natrolite, aegirine, K-feldspar, strontian apatite, titanite, sphalerite, barite and rare pyrrhotite and chalcopyrite. Electron-microprobe analysis gave SiO2 40.57, TiO2 18.87, Fe2O3 1.05, MnO 0.06, BaO 6.7, CaO 0.20, K2O 5.59, Nb2O5 10.49, SrO 0.08, Ta2O5 0.06, (H2O)calc 0.73, sum 97.83 wt.%. The amount of H2O was determined from crystal-structure analysis. There is one tetrahedrally coordinated Ti site, <T–O> 1.607 Å, occupied by Ti. There are two octahedrally coordinated sites, M(1), occupied by (Ti0.68 Nb0.15 Fe3+0.08 Zr0.04), with <M(1)–O> = 2.016 Å, and M(2), occupied by (Ti0.72 Nb0.15 Fe3+0.08)Za0.04 (Cl1,Cl2), with <M(2)–O> = 1.999 Å. The M(1) and M(2) sites are separated by 0.477 Å, and hence cannot be occupied simultaneously at a local level. There are three interstitial A sites: the A(1) site is [9]-coordinated and is occupied by (K0.66 Ba0.23 Na0.07 Ca0.02), with <A(1)–O> = 2.952 Å; the A(2) site is [8]-coordinated and is occupied by K, with <A(2)–O> = 2.861 Å, and the A(3) site is [6]-coordinated and is occupied by Na, with <A(3)–O> = 2.493 Å. Shcherbakovite is a K-analogue of batisite, ideally Ba Na2 Ti4+2 O2 [Si4O12]. Shcherbakovite is related to batisite by substitution of K for Ba and K for Na. “Noonkanbahite”, ideally Ba K Na Ti4+2 O2 [Si4O12], has never been approved by the IMA as a new mineral species. Based on the crystal chemistry of this structure type, the general formula of these minerals may be written as A B C M2 O [Si4O12], with the following end-member compositions: batisite, A = Ba, B = Na, C = Na; shcherbakovite, A = K, B = K, C = Na; “noonkanbahite”, A = Ba, B = K, C = Na; unnamed, A = K, B = Na, C = Na.

Keywords: shcherbakovite, batisite, end-member, crystal-structure refinement.

SOMMAIRE

Nous avons affiné la structure cristalline de la shcherbakovite provenant du mont Rasvumchorr, complexe alcalin de Khibina, péninsule de Kola, en Russie, dont la composition idéale est K2 Na Ti4+2 O (OH) [Si4O12], a 8.1538(4), b 10.5569(5), c 13.9882(6) Å, V 1204.1(2) Å3, groupe spatial Imma, Z = 4, Dcalc 3.194 g/cm3, jusqu'à un résidu R1 = 3.2% pour 960 réflexions uniques (F0 > 4σ(F)) prélevées sur monocristal avec un diffractomètre Bruker P4 muni d'un détecteur CCD (rayonnement MoKa). On trouve la shcherbakovite dans des veins hydrothermales tardives de natrolite à faible pendent, en association avec natrolite, aégrine, feldspath potassique, apatite strontiante, titane, barite et rare pyrrhotite et chalcopyrite. Les analyses à la microsonde électronique ont donné SiO2 40.57, TiO2 18.87, Fe2O3 1.05, MnO 0.06, BaO 6.7, CaO 0.20, K2O 5.59, Nb2O5 10.49, SrO 0.08, ZrO2 0.84, Ta2O5 0.06, (H2O)calc 0.73, somme 97.83% (poids). La quantité de H2O a été déterminée par échelle de la structure cristalline. Il y a un site à coordonnée tétraédrique, M(1), qu'occupe (K0.66 Nba0.23 Na0.07 Ca0.02), avec <M(1)–O> = 2.016 Å, et M(2), qu'occupe (Ti0.72 Nb0.15 Fe3+0.08)Za0.04 (Cl1,Cl2), avec <M(2)–O> = 1.999 Å. Les sites M(1) et M(2) sont 0.477 Å l'un de l'autre, et donc ne pourraient pas être remplis simultanément à un échelle locale. Il y a trois sites interstitiels: A: Le site A(1) possède une coordonnée [9] et contient (K0.66 Nba0.23 Na0.07 Ca0.02), avec <A(1)–O> = 2.952 Å; le site A(2) possède une coordonnée [8], et contient le K, avec <A(2)–O> = 2.861 Å, tandis que le site A(3) a une coordonnée [6], et contient le Na, avec <A(3)–O> = 2.493 Å. La shcherbakovite est l'analogue à dominance de K de la batisite, dont la formule idéale est Ba Na Ti4+2 O2 [Si4O12]. Dans la shcherbakovite, il y a remplacement du Ba et du Na par le K. La “noonkanbahite”, dont la formule idéale serait Ba K Na Ti4+2 O2 [Si4O12], n'a pas été

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On the basis of a piezoelectric effect, they chose the crystal structure of batisite. Belov (1962) solved the crystal structure of batisite, (Ba, Ca, Mn, Sr)\((K0.70 \ Na0.30) \ Na(Ti1.72 \ Fe0.16 \ Zr0.06)\)Å3, using the space group \(O_{12}^\parallel\), from Tertiary nephelinite–leucite volcanic rocks of the Inagli complex, Aldan, Siberia; subsequently recognized as a rock-forming mineral in low-temperature zeolite paragenesis at Khibina complex (Khomyakov 1995), in which the semicircular rischorrite zone is one of the major constituents.

The Ba–Na analogue of shcherbakovite, batisite, was subsequently recognized as a rock-forming mineral in peralkaline rocks of the Inagli complex, Aldan, Siberia; Kravchenko et al. (1960) reported that shcherbakovite, (Ba, Ca, Mn, Sr)\(20.92 \ K \ Na(Ti1.68 \ Fe0.14 \ Zr0.09)\)Å2, 02 \ (O1.66(OH)0.34)\)Si4\(O_{12}\), and shcherbakovite form a solid-solution series with the following isomorphic scheme: \(Ba + Ti^{4+} \leftrightarrow K(Na) + Nb\). However, we note that neither shcherbakovite nor batisite contain essential Nb, and hence this scheme cannot be correct. Nikitin & Belov (1962) solved the crystal structure of batisite. On the basis of a piezoelectric effect, they chose the space group \(Imma_2\), \(a\ 10.40, b\ 13.85, c\ 8.10\) Å, \(V\ 1166.7\) Å3, \(Z\ 4\).

Yakovlevskaya & Efimov (1963) provided additional crystallographic data on the shcherbakovite–batisite series. Prider (1965) described a K–Ba–Ti silicate, (Ba0.55 K0.20 Ca0.18 Ti1.99 O2.00)\(\left[Si_{4}O_{12}\right]\), under the name “noonkanbahite”, but it was not approved by the IMA. Schmahl & Tillmanns (1987) refined the crystal structure of batisite, (Ba0.60 K0.40)\(\left[Si_{4}O_{12}\right]\)\(\left[Si_{4}O_{12}\right]\)\(\left[Si_{4}O_{12}\right]\), from Tertiary nepheline–leucite volcanic rocks from Westeifel, Germany. There was no second harmonic-generation response for a single crystal, and they used the space group \(Imma\); attempts to refine the structure in \(Imma_2\) were unsuccessful (Schmahl & Tillmanns 1987). On the other hand, Rastsvetaeva et al. (1997) refined K-rich batisite in the space group \(Imma_2\).

Currently, minerals of the shcherbakovite–batisite series have been described from a range of (K,Na)-rich to ultrapotassic silica-undersaturated rocks considered to be of mantle origin. Shcherbakovite–batisite minerals of intermediate composition have been described from pneumatolitic parageneses lining vesicles in Si-rich lamproites of the Leucite Hills, Wyoming (Mitchell 1990), as inclusions in “samidine derived from leucite” in a lamproite dyke in Baffin Island, Canada (Hogarth 1997), and as a mineral common in lamproite pegmatites at the Walgidge Hills, western Kimberley, Australia (Prider 1965). Crystallization of shcherbakovite in a low-temperature zeolite paragenesis at Khibina indicates that a very wide \(P–T\) range of stability can be expected for the members of the group. The structure of these minerals is tolerant to a wide range of isomorphic substitutions at the cation sites. This structural flexibility allows shcherbakovite–batisite to be a sink for high field-strength and large-ion lithophile elements in parageneses ranging from mantle conditions to postmagmatic evolution of peralkaline rocks in the upper lithosphere.

Here, we report on the crystal structure of shcherbakovite from Mount Rasvumchorn, Khibina massif, Kola Peninsula, Russia and the crystal chemistry of the mineral association.

### OCCURRENCE AND MINERAL ASSOCIATION

Shcherbakovite has been found at the northwestern ridge of Mount Rasvumchorn, in shallowly dipping hydrothermal veins of semitransparent columnar natrolite. The veins vary from 3 to 20 cm in thickness and cut poikilitic syenites, described by Kozyreva et al. (1990) as a kalsilite–nepheline-bearing ultrapotassic variety of rischorrite. The veins have selvages 3–5 cm wide composed of green acicular aegirine and yellow potassium feldspar. Shcherbakovite forms prismatic crystals ranging from a few mm to 6 cm in length (Fig. 1), embedded in natrolite. The paragenesis includes relatively large well-shaped single prisms of black aegirine–diopside, slightly corroded blocky orthoclase, euhedral 1–2 cm crystals of strontian fluorapatite (SrO 18.7–22.3, F up to 4.2 wt.%), anhedral colorless titane (cores of grains contain up to 8.6 wt.% ZrO\(_2\), 5.6 wt.% Nb\(_2\)O\(_5\))
and 1.1 wt.% Al$_2$O$_3$), and rare grains of pyrrhotite and chalcopyrite and laths of manganoo pectolite up to 20 cm in length, which in places have been completely replaced by a fine-grained mixture of Fe–Mn oxides.

The majority of the shcherbakovite-bearing veins were affected by faulting along their axial zones, and were injected by additional hydrothermal solutions, which resulted in deposition of spherulites of baryllite 1–5 mm in diameter and caused fragmentation of crystals and coating of large shcherbakovite crystals by an unidentified enamel-like yellowish silicate phase, in addition to the alteration of Mn-rich pectolite, titanite and apatite. The most homogeneous and transparent crystals of shcherbakovite occur on slightly corroded surfaces of K-feldspar. One representative crystal, 1.5 mm in length, was broken and a fragment was selected for single-crystal structure refinement.

X-RAY DATA COLLECTION AND STRUCTURE REFINEMENT

X-ray-diffraction data for shcherbakovite were collected with a Bruker P4 diffractometer equipped with a SMART 1K CCD detector (MoK$_\alpha$ radiation) from a single crystal of shcherbakovite with dimensions 0.30 × 0.08 × 0.08 mm. The intensities of 5645 reflections with $1<|h|<11$, $1<|k|<14$, $1<|l|<18$ were collected to 59.99° 20 using 25 s per 0.125° frame: an empirical absorption-correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters were obtained from 1632 reflections with $I > 10\sigma(I)$. Using atom coordinates of batisite (Schmahl & Tillmanns 1987), the crystal structure of shcherbakovite was refined to $R_1 = 0.032$ and a GoF value of 1.325 for 986 independent reflections (76 refined parameters including extinction) with the Bruker SHELXTL version 5.1 system of programs.

In the course of the refinement, the $M$ site was characterized by a high value of the displacement parameter along the $a$ axis ($U_{11} = 0.09$). A difference-Fourier map revealed a maximum of 4.5 e located 0.51 Å from the $M$ site. This maximum was included in the refinement as the $M(2)$ site, and the initial $M$ site was relabeled as $M(1)$. Site occupancies were refined for the two $M$ sites (occupied primarily by Ti and Nb) and three $A$ sites (occupied primarily by K, Ba and Na).

Details of the data collection and structure refinement are given in Table 1, final atom-parameters are given in Table 2, selected interatomic distances and angles in Table 3, refined site-scattering values and assigned populations for selected sites are given in Table 4, and bond-valence values are given in Table 5. A structure-factor table may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

CHEMICAL COMPOSITION

After collecting the X-ray-diffraction data, the crystal of shcherbakovite was polished and analyzed with a Cameca SX 100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of

![Fig. 1. Secondary electron image of shcherbakovite crystal.](image-url)
15 kV, a specimen current of 20 nA, a beam size of 20 μm and count times on peak and background of 20 and 10 s, respectively. The following standards and crystals were used for K, L or M X-ray lines: Na: albite, Si: diopside, Mg: Al: spinel, K: orthoclase, Ti: titanite, Ba: barite, Mn: spessartine, Nb: LiNbO₃, Sr: SrTiO₃, Zr: zircon, Fe: fayalite, and Ta: manganotantalite. Data were reduced using the φ(2θ) procedure (Merlet 1992). The amount of H₂O was calculated from the structure refinement. Table 6 gives the chemical composition and empirical formula unit based on 14 anions including 0.48 OH groups pfu (per formula unit): (K₀.₆₆ Ba₀.₂₃ Na₀.₀₇ Ca₀.₀₂)O₁.₄₅ Ti₁.₄₀ Nb₀.₄₇ Fe³⁺₀.₀₈ Zr₀.₀₄ O₁.₅₂ OH₀.₄₈ S₁₂.₀₀ [Si₄ O₁₂].

### Table 1: Miscellaneous Refinement Data for Shcherbakovite

<table>
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<th>Parameter</th>
<th>Value</th>
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<td>a (Å)</td>
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<tr>
<td>b</td>
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<td>c</td>
<td>13.8562(9)</td>
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<td>Imma</td>
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<td>Z</td>
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<td>Absorption coefficient</td>
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<td>F(000)</td>
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<tr>
<td>Density (g/cm³)</td>
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<tr>
<td>Crystal size (mm)</td>
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<tr>
<td>Radiation filter</td>
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<td>2θ-range for data collection (°)</td>
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<td>R(int) (%)</td>
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<td>Relections collected</td>
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<tr>
<td>Independent reflections</td>
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<tr>
<td>F &gt; 4σF</td>
<td>960</td>
</tr>
<tr>
<td>Refinement method</td>
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<tr>
<td>Goodness of fit on F²</td>
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<tr>
<td>Final R, wR (%)</td>
<td>R₁ = 3.18, wR₂ = 8.62</td>
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### Table 2: Final Atom Positions and Displacement Parameters for Shcherbakovite

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<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U₁₁</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₄₄</th>
<th>U₅₅</th>
<th>U₆₆</th>
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<td>0.0155(17)</td>
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<td>0.0074(4)</td>
<td>0.005(5)</td>
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<td>M(2)</td>
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<td>0.7458(5)</td>
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<td>0.0168(4)</td>
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<td>0.0009(3)</td>
<td>0.0009(3)</td>
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<td>O(2)</td>
<td>0</td>
<td>3/4</td>
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<td>0.0287(7)</td>
<td>0.0035(20)</td>
<td>0.0127(11)</td>
<td>0.0102(11)</td>
<td>0.0102(11)</td>
<td>0.0102(11)</td>
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</table>

### Cation Sites

In the crystal structure of shcherbakovite, there is one T site occupied by Si with Si–O = 1.607 Å. There are two M sites, M(1) and M(2), partly occupied by Ti and Nb, with M(1)–M(2) = 0.477 Å, and hence only one of these two sites can be locally occupied. The M(1) site is occupied by (Ti₀.₆₈ Nb₀.₃₂ O₁.₃₁) with <M(1)–O> = 2.016 Å, and the M(2) site is occupied by (Ti₀.₇₂ Nb₀.₁₅ O₁.₅₈) with <M(2)–O> = 1.999 Å. This splitting of the M site is in accord with the results of Schmahl & Tillmanns (1987). Although they reported only a single (non-split) M site, one of the displacement parameters is (on average) fifteen times larger than the other two displacement parameters for this site.

There are three interstitial A sites: the A(1) site is occupied by (K₀.₆₆ Ba₀.₂₃ Na₀.₀₇ Ca₀.₀₂), the A(2) site is occupied by K, and the A(3) site is occupied by Na. In previous structural studies of batisite, the A(1), A(2) and A(3) sites are described as [12]-, [11]- and [10]-coordinated by Schmahl & Tillmanns (1987) and Rastsvetaeva et al. (1997), and [12]-, [11]- and [9]-coordinated by Nikitin & Belov (1962). For the coordination numbers [12], [11] and [10], the incident bond-valence sums at the A(1), A(2) and A(3) sites in shcherbakovite are 1.118, 1.129 and 1.142 valence units (vu), respectively, and the ideal values, derived from the site populations of Table 4, are 1.26, 1.00 and 1.00 vu. Examining the bond-valence sums around the anions (Table 5) indicates that the sum at the O(4) anion is somewhat high at 2.25 vu. There are several long A–O distances in shcherbakovite (Fig. 2); should these be considered as chemical bonds? Inspection of Table 5 indicates that there are five distances that involve bond valences in the range 0.03–0.050 vu. If we wish to discount any of these distances as bonds, we must discount all of these distances as bonds. If this is done, the corresponding incident bond-valence sums at A(1), A(2) and A(3) are 1.000, 1.004 and 0.998 vu, and the sum at the O(4) site is 2.14 vu.
These values indicate that the coordination numbers of the A\(_1\), A\(_2\) and A\(_3\) sites are [9], [8] and [6], respectively, rather than [12], [11] and [10] or [9]. Similar calculations for batisite also indicate that the coordination numbers of the A\(_1\), A\(_2\) and A\(_3\) sites are [9], [8] and [6].

**Topology of the structure**

In the structure of shcherbakovite, [Si\(_4\)O\(_{12}\)]~8– tetrahedra link together to form an [Si\(_4\)O\(_{12}\)]~8– chain first described in batisite (Nikitin & Belov 1962). This chain extends along the \(a\) axis (Fig. 2a), and (TiO\(_6\)) octahedra link via common vertices to form straight [TiO\(_5\)]~6– chains extending along the \(a\) axis (Fig. 3a). These two types of chains, [Si\(_4\)O\(_{12}\)]~8– and [TiO\(_5\)]~6–, link together to form a mixed tetrahedron–octahedron framework (Fig. 3b). Each [TiO\(_6\)] octahedron is connected through common vertices to four (SiO\(_4\)) tetrahedra, and each (SiO\(_4\)) tetrahedron is connected to two octahedra and two tetrahedra.

There are three types of interstitial cages (Fig. 3b), and they are significantly different in size. The largest cage includes the A\(_1\) site and is populated by K, Ba, Na and minor Ca and Sr. The intermediate-sized cage...
includes the A(2) site, and is occupied by K. The smallest cage includes the A(3) site and is occupied by Na.

The O(6) site

Calculation of the bond valence incident at O(6) in shcherbakovite gives 1.52 $\text{vu}$ (Table 5). This calculation gives rise to two possibilities: (1) there is a symmetrical hydrogen bond or strong bi- or trifurcated hydrogen bonds, or (2) the O(6) site is partly occupied by (OH)$^-$ and O$^{2-}$. The site content of (0.52 O$^{2-}$ + 0.48 OH$^-$) that is required for electroneutrality gives a value of $(\text{H}_2\text{O})_{\text{calc}}$ of 0.73 wt.% (Table 6).

Splitting of the M site

We attempted to change the space group or origin (or both) of the structure to produce a single M site, but were unable to do so; hence we are forced to conclude that the splitting of the M site [to produce the M(1) and M(2) sites] is real. This splitting is presumably related to the occupancy of the O(6) site [and possibly the O(5) site] by both O$^{2-}$ and (OH)$^-$. The local bond-valence situation for each case is shown in Figure 4. Where the bridging anion [O(br)] is O$^{2-}$, the $M$–O(br) bond-valences must be $\sim$1.0 $\text{vu}$, whereas where the bridging anion is (OH)$^-$, the $M$–O(br) bond-valences must be $\sim$0.5 $\text{vu}$; this arrangement may be modified slightly by the presence of the A(1)–O(5) bond, but we may ignore this (weak) bond for simplicity. As is apparent in Figure 4, O$^{2-}$ and (OH)$^-$ anions will tend to alternate along the [Ti$^{4+}$]$_2$ chain. So why does this pattern of order not produce a change in cell dimension or space group? Examination of Figure 3 shows that the [Ti$^{4+}$]$_2$ chains do not link to each other; they are separated by silicate chains. Hence adjacent [Ti$^{4+}$]$_2$ chains may adopt configurations with respect to O$^{2-}$–(OH)$^-$ order that are not coupled to each other. This random disorder results in an average structure in which the $M$–O$^{2-}$ and $M$–(OH)$^-$ configurations overlap, with an apparent 50:50 splitting of the M site to produce the M(1) and M(2) sites observed here.

This splitting of the M site produces a complication in assigning the site populations, as at short range, where one of the sites is occupied, the locally associated site must be vacant. As noted above, the amount of splitting is controlled by the amount of O$^{2-}$ and (OH)$^-$ at the bridging O(6) site, which is approximately 1:1 in this crystal. Thus the M(1) and M(2) sites will be each approximately half-occupied, which means that the dominant species at each site is a vacancy (Table 4). From a crystallographic perspective, which includes issues of short-range order, the M(1) and M(2) sites are distinct, whereas from the perspective of writing a chemical formula, the M(1) and M(2) sites need to be combined into one aggregate site that is then completely occupied (cf. Tables 4 and 6).

**DISCUSSION**

In Table 7, we summarize selected crystallographic data for the minerals of the shcherbakovite–batisite group. Structure refinements for batisite have been done in space groups $Ima_2$ and $Imam$. In this work, we have used the space group $Imma$ (standard setting). In Table 7, all formulae are given in a structurally appropriate fashion. A(1) is occupied by large cations K and Ba, A(2) is occupied solely by K or (K + Na), and A(3)
is occupied solely by Na ($^{(9)}$Ba = 1.47, $^{(9)}$K = 1.55, $^{(8)}$K = 1.51, $^{(6)}$Na = 1.02 Å; Shannon 1976).

Using the criteria of Hawthorne (2002) for an end member, we can propose four end-members for the shcherbakovite–batisite solid-solution series:

**Batisite**  
Ba Na Na Ti$_2$O$_2$ [Si$_4$O$_{12}$]

**Shcherbakovite**  
K Na Na Ti$_2$O(OH) [Si$_4$O$_{12}$]

**“Noonkanbahite”**  
Ba K Na Ti$_2$O$_2$ [Si$_4$O$_{12}$]

**Unnamed**  
K Na Na Ti$_2$O(OH) [Si$_4$O$_{12}$]

All formulae are neutral, they are compatible with the crystal structure of these minerals, their composition is fixed, and a maximum of one site contains two species in a fixed amount.

“**Noonkanbahite**” is not accepted as a valid mineral species, but according to our considerations, it should be regarded as such. Rastsvetaeva et al. (1997) investigated the crystal structure of K-containing batisite and gave the structural formula as (Ba$_{0.7}$Ca$_{0.1}$Sr$_{0.2}$) K Na [Ti$_{4+}$ (Ti$_{4+}$0.6 Fe$_{3+}$0.4)] (O,OH)$_2$ [Si$_4$O$_{12}$]; this formula corresponds to the chemical composition of “noonkanbahite”, ideally Ba K Na Ti$_{4+}$2 O$_2$ [Si$_4$O$_{12}$] (Prider 1965).

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**TABLE 5. BOND-VALENCE TABLE FOR SHCHERBAKOVITE**

<table>
<thead>
<tr>
<th>A(1)**</th>
<th>A(2)**</th>
<th>A(3)**</th>
<th>M(1)**</th>
<th>M(2)**</th>
<th>Z*</th>
<th>Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)</td>
<td>+0.135</td>
<td>+0.206</td>
<td>&lt;0.035</td>
<td>&lt;0.213</td>
<td>1.053</td>
<td>2.07</td>
</tr>
<tr>
<td>O(2)</td>
<td>+0.115</td>
<td>+0.098</td>
<td>+0.348</td>
<td>+0.304</td>
<td>1.000</td>
<td>1.93 [1.96]</td>
</tr>
<tr>
<td>O(3)</td>
<td>&lt;0.034</td>
<td>&lt;0.040</td>
<td>0.917</td>
<td>0.917</td>
<td>2.17</td>
<td></td>
</tr>
<tr>
<td>O(4)</td>
<td>0.346</td>
<td>0.046</td>
<td>0.089</td>
<td>0.052</td>
<td>1.68 [1.73]</td>
<td></td>
</tr>
<tr>
<td>O(5)</td>
<td>0.090</td>
<td>0.145</td>
<td>0.145</td>
<td>0.145</td>
<td>1.49 [1.52]</td>
<td></td>
</tr>
<tr>
<td>Σ</td>
<td>1.000</td>
<td>1.000</td>
<td>0.986</td>
<td>2.164</td>
<td>1.681</td>
<td>4.162</td>
</tr>
</tbody>
</table>

* bond-valence parameters (v) from Brown (1981);  
* values in [ ] calculated for A(1), A(2), A(3) coordination numbers [12, 11] and [10], respectively.

---

**TABLE 6. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (apfu) FOR SHCHERBAKOVITE**

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>Nb$_2$O$_5$</th>
<th>ZrO$_2$</th>
<th>BaO</th>
<th>Nb</th>
<th>K$_2$O</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>H$_2$O**</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
<th>Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shcherbakovite</td>
<td>40.57</td>
<td>18.87</td>
<td>1.05</td>
<td>10.49</td>
<td>0.84</td>
<td>6.07</td>
<td>0.20</td>
<td>5.59</td>
<td>0.73</td>
<td>0.23</td>
<td>97.63</td>
<td>0.06</td>
<td>0.07</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Noonkanbahite</td>
<td>40.87</td>
<td>19.20</td>
<td>1.15</td>
<td>10.67</td>
<td>0.91</td>
<td>6.23</td>
<td>0.21</td>
<td>5.72</td>
<td>0.75</td>
<td>0.24</td>
<td>97.98</td>
<td>0.07</td>
<td>0.08</td>
<td>1.01</td>
<td>1.03</td>
</tr>
</tbody>
</table>

---

**TABLE 7. CRYSTAL DATA FOR MINERALS WITH GENERAL FORMULA A$_m$B$_n$C$_p$M$_q$(O,OH)$_r$[Si$_4$O$_{12}$]**

<table>
<thead>
<tr>
<th>Mineral and Formula</th>
<th>Space group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$\alpha$-O$^-$ (Å)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shcherbakovite</td>
<td>(1) K$<em>2$(Ba$</em>{0.7}$Ca$<em>{0.1}$Sr$</em>{0.2}$)Ba$<em>{0.5}$K$</em>{0.5}$Ti$_2$O$_2$(OH)$_2$[Si$<em>4$O$</em>{12}$]</td>
<td>P2$_1$2$_1$2$_1$</td>
<td>8.153(4)</td>
<td>10.566(5)</td>
<td>13.978(6)</td>
<td>1.43</td>
</tr>
<tr>
<td>(2) K$<em>2$(Ba$</em>{0.7}$Ca$<em>{0.1}$Sr$</em>{0.2}$)Ba$<em>{0.5}$K$</em>{0.5}$Ti$_2$O$_2$(OH)$_2$[Si$<em>4$O$</em>{12}$]</td>
<td>P2$_1$2$_1$2$_1$</td>
<td>8.156(4)</td>
<td>10.566(5)</td>
<td>13.978(6)</td>
<td>1.43</td>
<td>S</td>
</tr>
<tr>
<td>(3) K$<em>2$(Ba$</em>{0.7}$Ca$<em>{0.1}$Sr$</em>{0.2}$)Ba$<em>{0.5}$K$</em>{0.5}$Ti$_2$O$_2$(OH)$_2$[Si$<em>4$O$</em>{12}$]</td>
<td>P2$_1$2$_1$2$_1$</td>
<td>8.162(4)</td>
<td>10.566(5)</td>
<td>13.978(6)</td>
<td>1.43</td>
<td>S</td>
</tr>
<tr>
<td>Batistsite</td>
<td>(1) Ba$<em>{0.5}$K$</em>{0.5}$Ti$_2$O$_2$(OH)$_2$[Si$<em>4$O$</em>{12}$]</td>
<td>P2$_1$2$_1$2$_1$</td>
<td>8.134(5)</td>
<td>13.850(5)</td>
<td>8.06</td>
<td>1.43</td>
</tr>
<tr>
<td>(2) Ba$<em>{0.5}$K$</em>{0.5}$Ti$_2$O$_2$(OH)$_2$[Si$<em>4$O$</em>{12}$]</td>
<td>P2$_1$2$_1$2$_1$</td>
<td>8.134(5)</td>
<td>13.850(5)</td>
<td>8.06</td>
<td>1.43</td>
<td>S</td>
</tr>
</tbody>
</table>

Schmahl & Tillmanns (1987) reported the crystal structure of batisite with the chemical formula (Ba$_{0.6}$ K$_{0.4}$) (K$_{0.7}$ Na$_{0.3}$) Na (Ti$_{4+}$1.72 Fe$_{3+}$0.16 Nb$_{0.06}$ Zr$_{0.06}$)$_2$ O$_2$ [Si$_4$O$_{12}$]. This “batisite” actually corresponds to the “noonkanbahite” formula indicated above. Furthermore, Mitchell (1990) reported the occurrence of shcherbakovite in leucite phlogopite lamproites from the Leucite Hills, Wyoming, and Hogarth (1997) reported shcherbakovite–batisite from leucite phlogopite lamproite dykes from southeastern Baffin Island, Canada, but the compositions reported correspond to that of “noonkanbahite” given above. We currently have a proposal submitted to the Commission on New Minerals and Mineral Names of the International Mineralogical Association for approval of “noonkanbahite” as a new mineral species.

Ba, K or Nb may be absent in natural examples, whereas Na and Ti always occur in excess of 0.8 and 1.3 apfu, respectively (Schmahl & Tillmanns 1987, this work). The excess of Si above the ideal value of 4, which commonly occurs in natural batisite and shcherbakovite, possibly reflects the presence of small amounts of unaccounted OH$^-$ groups (Es’kova & Kazakova 1954, Kravchenko et al. 1960, Prider 1965).

The principal substitutions by which additional cations are incorporated into this structure type are as follows:

$$Ba + Ti^{4+} \leftrightarrow (K,Na) + Nb$$

$$2Ti^{4+} \leftrightarrow Fe^{3+} + Nb$$

Schmahl & Tillmanns (1987) gave the general formula of the shcherbakovite–batisite minerals as $A_3 M_2$ O$_2$ [Si$_4$O$_{12}$]. On the basis of the structure of these minerals, it is more appropriate to write the formula as $A B C M_2 /H9278$ [Si$_4$O$_{12}$], where $A = Ba, K, Na, Ca; B = K, Na; C = Na, Ca; M = Ti^{4+}, Nb, Fe^{3+}, Zr; \phi = O, (OH)$.

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**REFERENCES**


HAWTHORNE, F.C. (2002): The use of end-member charge-ar-
rangements in defining new mineral species and hetero-
valent substitutions in complex minerals. Can. Mineral. 40,
699-710.

from Napoleon Bay, Baffin Island: multistage Proterozoic

KHOMYAKOV, A.P. (1995): Mineralogy of Hyperapatitic Alka-

KOZYREVA, L.V., KOROBENIKOFF, A.N. & MEN’SHIKOV, Yu.P.
(1990): New type of the ultrapotassic rocks in Khibina
complex. In News in Mineralogy of Karelia–Kola Region.
Karelija Branch AN USSR, Petrozavodsk, Russia (116-
129; in Russ.).

KRAVCHENKO, S.M., VLASOVA, E.V. & PINEVICH, N.G. (1960):
657-660 (in Russ.).

M ERCLET, C. (1992): Quantitative electron probe microanalysis:
new accurate φ(ρz) description. Mikrochim. Acta 12,
107-115.

MITCHELL, R.H. (1990): Shcherbakovite in leucite phlogopite
Mag. 54, 645-646.

NIKITIN, A.V. & BELOV, N.V. (1962): Crystal structure of
batisite Na3BaTi2Si4O14 = Na3BaTi2O2[Si4O12] . Dokl.
Akad. Nauk USSR 146, 142-143.

PRIDER, R.T. (1965): Noonkanbahite, a potassic batisite from
the lamproites of western Australia. Mineral. Mag. 34,
403-405.

RASTSVETAEVA, R.K., PUSHCHAROVSKII, D.YU., KONEV, A.A.
& EVSYUNIN, V.G. (1997): Crystal structure of K-contain-

SCHMAHL, W.W. & TILLMANN, E. (1987): Isomorphic substi-
tutions, straight Si–O–Si geometry, and disorder of tetra-
hedral tilting in batisite, (Ba,K)(K,Na)Na(Ti,Fe,Nb,Zr)

SHANNON, R.D. (1976): Revised effective ionic radii and system-

Göttingen, Göttingen, Germany.

SOKOLOVA, M.N., BUKOVA, T.A. & RUDNITSKAYA, E.S. (1964):
Mineral. Obshchest. 93, 641-654 (in Russ.).

YAKOVLEVSKAYA, T.A. & EFIMOV, A.F. (1963): New data on
crystallography of batisite–shcherbakovite-series minerals.

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