

NEW
MINERALS

Batisivite, $V_8Ti_6[Ba(Si_2O)]O_{28}$, a New Mineral Species from the Derbylite Group¹

L. Z. Reznitsky^a, E. V. Sklyarov^a, T. Armbruster^b, E. V. Galuskin^c, Z. F. Ushchapovskaya^a,
Yu. S. Polekhovskiy^d, N. S. Karmanov^e, A. A. Kashaev^a, and I. G. Barash^a

^a*Institute of the Earth's Crust, Siberian Branch, Russian Academy of Sciences, ul. Lermontova 128, Irkutsk, 664033 Russia*

^b*Bern University, Friestrasse 3, Bern, CH-3012, Switzerland*

^c*Department of Earth Sciences, University of Silesia, ul. Bendzinska 60, Sosnowiec, 41-200 Poland*

^d*Faculty of Geology, St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 199034 Russia*

^e*Geological Institute, Siberian Branch, Russian Academy of Sciences, ul. Sakh'yanovoi 6, Ulan-Ude, 670042 Russia*

Received March 29, 2007

Abstract—Batisivite has been found as an accessory mineral in the Cr–V-bearing quartz–diopside metamorphic rocks of the Slyudyanka Complex in the southern Baikal region, Russia. A new mineral was named after the major cations in its ideal formula (Ba, Ti, Si, V). Associated minerals are quartz, Cr–V-bearing diopside and tremolite; calcite; schreyerite; berdesinskiite; ankangite; V-bearing titanite; minerals of the chromite–coulsomite, eskolaite–karelianite, dravite–vanadiumdravite, and chernykhite–roscoelite series; uraninite; Cr-bearing goldmanite; albite; barite; zircon; and unnamed U–Ti–V–Cr phases. Batisivite occurs as anhedral grains up to 0.15–0.20 mm in size, without visible cleavage and parting. The new mineral is brittle, with conchoidal fracture. Observed by the naked eye, the mineral is black and opaque, with a black streak and resinous luster. Batisivite is white in reflected light. The microhardness (VHN) is 1220–1470 kg/mm² (load is 30 g), the mean value is 1330 kg/mm². The Mohs hardness is near 7. The calculated density is 4.62 g/cm³. The new mineral is weakly anisotropic and birefracted. The measured values of reflectance are as follows (λ , nm— R'_{\max}/R'_{\min}): 440—17.5/17.0; 460—17.3/16.7; 480—17.1/16.5; 500—17.2/16.6; 520—17.3/16.7; 540—17.4/16.8; 560—17.5/16.8; 580—17.6/16.9; 600—17.7/17.1; 620—17.7/17.1; 640—17.8/17.1; 660—17.9/17.2; 680—18.0/17.3; 700—18.1/17.4. Batisivite is triclinic, space group $P\bar{1}$; the unit-cell dimensions are: $a = 7.521(1)$ Å, $b = 7.643(1)$ Å, $c = 9.572(1)$ Å, $\alpha = 110.20^\circ(1)$, $\beta = 103.34^\circ(1)$, $\gamma = 98.28^\circ(1)$, $V = 487.14(7)$ Å³, $Z = 1$. The strongest reflections in the X-ray powder diffraction pattern [d , Å (I , %)(hkl)] are: 3.09(8)(12 $\bar{2}$); 2.84, 2.85(10)(021, 120); 2.64(8)(21 $\bar{3}$); 2.12(8)(31 $\bar{3}$); 1.785(8)(32 $\bar{4}$), 1.581(10)(24 $\bar{2}$); 1.432, 1.433(10)(322, 124). The chemical composition (electron microprobe, average of 237 point analyses, wt %) is: 0.26 Nb₂O₅, 6.16 SiO₂, 31.76 TiO₂, 1.81 Al₂O₃, 8.20 VO₂, 26.27 V₂O₃, 12.29 Cr₂O₃, 1.48 Fe₂O₃, 0.08 MgO, 11.42 BaO; the total is 99.73. The VO₂/V₂O₃ ratio has been calculated. The simplified empirical formula is $(V_{4.8}^{3+}Cr_{2.2}V_{0.7}^{4+}Fe_{0.3})_{8.0}(Ti_{5.4}V_{0.6}^{4+})_{6.0}[Ba(Si_{1.4}Al_{0.5}O_{0.9})]O_{28}$. An alternative to the title formula could be a variety (with the diorthogroup Si₂O₇) $V_8Ti_6[Ba(Si_2O_7)]O_{22}$. Batisivite probably pertains to the $V_8^{3+}Ti_6^{4+}[Ba(Si_2O)]O_{28}$ — $Cr_8^{3+}Ti_6^{4+}[Ba(Si_2O)]O_{28}$ solid solution series. The type material of batisivite has been deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow.

DOI: 10.1134/S1075701508070076

INTRODUCTION

Reznitsky et al. (2001), having described a new mineral species vanadiumdravite from metamorphic rocks of the Slyudyanka Complex, mentioned the presence of unknown Cr-bearing titanium–vanadium oxides associated with the new mineral. The subsequent detailed description of fractions of ore minerals allowed the

identification of two Ba–Ti–V(Cr) oxides along with Ti–V(Cr) oxides in one of the samples. One of these oxides turned out to be the rare mineral ankangite Ba(Ti,V,Cr)₈O₁₆ (the first finding in Russia), while another, a new mineral species from the derbylite group with the ideal formula $V_8Ti_6[Ba(Si_2O)]O_{28}$, described in this study. The name batisivite was given after the major cations in the ideal formula (Ba, Ti, Si, V).

MODE OF OCCURRENCE AND PHYSICAL PROPERTIES

The Cr–V-bearing metamorphic rocks of the Slyudyanka Complex have been characterized many times,

¹ Considered and recommended by the Commission on New Minerals and Mineral Names, Russian Mineralogical Society. Approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association February 28, 2007 (IMA no. 2006-054).

Corresponding author: L. Z. Reznitsky. E-mail: garry@crust.irk.ru

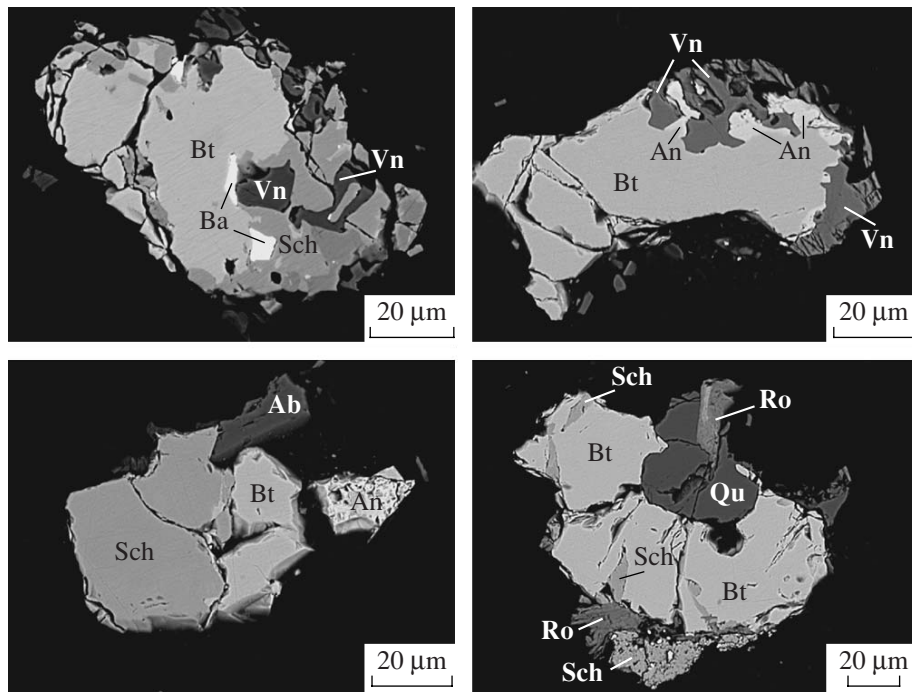


Fig. 1. Mineral assemblages with participation of batisivite, BSE images. (Bt) batisivite, (Sch) schreyerite, (Ba) barite, (Vn) vanadiumdravite, (An) ankangite, (Ab) albite, (Ro) roscoelite, (Qu) quartz.

when new and rare minerals of Cr and V identified in the rocks were described. The complete characteristics of these rocks were given by Vasil'ev et al. (1981) and Konev et al. (2001).

Batisivite was found as an accessory mineral in a sample of bedded–banded quartz–diopside rock consisting of alternating wide (2–5 cm) bands or layers of quartz or substantially diopside composition with an admixture of tremolite and calcite. Diopside and retrograde metamorphic tremolite pertain to Cr–V-bearing varieties; the absolute majority of Cr and V minerals proper, including batisivite, are inclusions in bands of gray and dark fine- to medium-grained or massive quartz.

Due to the extremely small amount of the new mineral, difficulties were encountered in studying the specimen prepared directly from rock. Batisivite was concentrated in the heavy electromagnetic fraction, which was examined with an electron microscope equipped with an energy dispersive spectrometer (EDS), and in polished sections with electron microprobe. About 200 grains and intergrowths of the mineral were identified and examined. In addition to rock-forming quartz, associated minerals are Cr–V-bearing diopside and tremolite; calcite; schreyerite; berdesinskiite; V-bearing titanite; ankangite; spinels of the chromite–coulsonite series; an Fe-bearing oxides of the eskolaite–karelianite series; uraninite; micas of the chernykhite–roscoelite series; Cr-bearing goldmanite; and tourmalines of the dravite–vanadiumdravite, albite, barite, zir-

con, and unnamed phases (U–Ti–V, Ti–V, and V–Cr oxides). Batisivite is closely intergrown with most of these minerals. Typical examples are shown in Fig. 1.

The new mineral occurs as isometric and elongated (ellipsoidal) anhedral grains with a maximum size of 150–200 µm (Fig. 2). The sporadic faces that proved impossible to identify are observable on certain grains. In addition, a single fragment of prismatic crystal with unclear faces was found (Fig. 2). Cleavage was not observed. In megascopic appearance and under a binocular microscope, batisivite is black, with a black streak (powder) and resinous luster. The fracture is conchoidal. The new mineral is brittle. The microhardness (VHN) is 1200–1470 kgf/mm², the mean value (seven indentations in five grains) is 1330 kgf/mm², which corresponds to a Mohs hardness of 7.0–7.5. The microhardness was measured with a UI PMT-3 microhardness tester; loading was 30 g because of grain cracking under a higher load. Due to the small sizes of impressions (6–7 µm diagonal), the accuracy of measurements is not high. The density calculated from the X-ray diffraction data is 4.62 and 4.64 g/cm³ for two grains of different composition.² The density of batisivite calculated for the average composition from the measured volume of a unit cell determined on the basis of X-ray single crystal data (see below) is 4.624 g/cm³. The new mineral is separated into an electromagnetic fraction by magnetic separators at a moderate current intensity, is

² The compositions of grains are listed in Table 3.

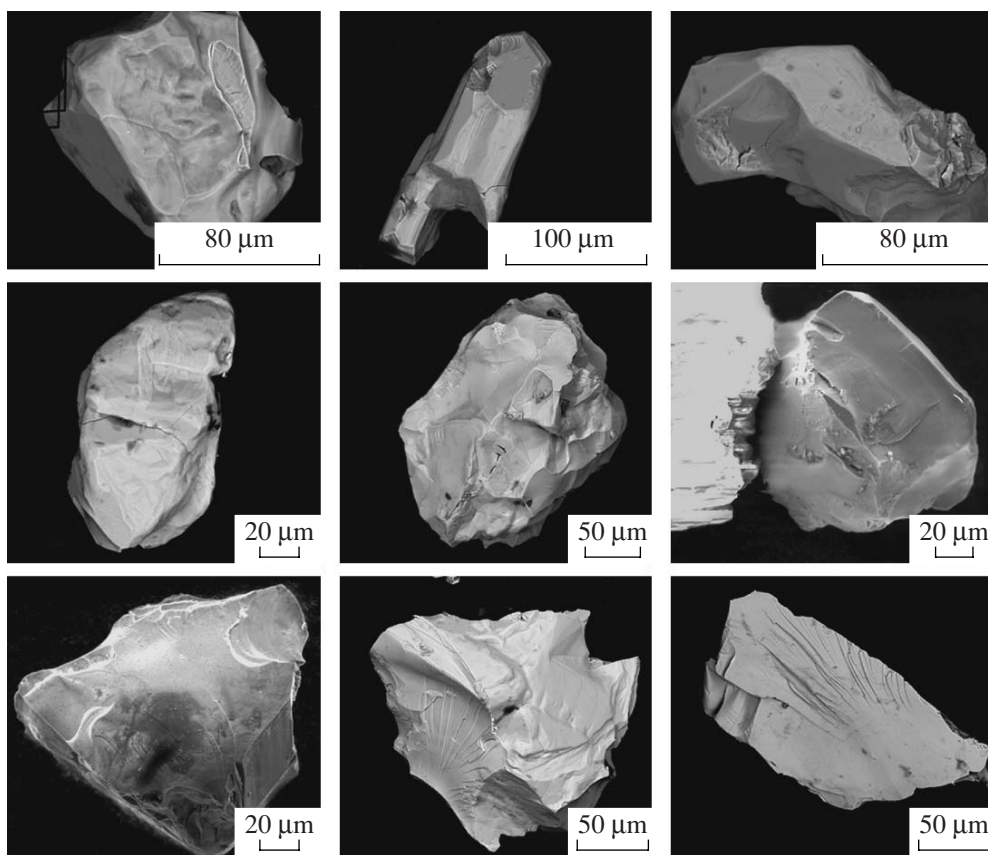


Fig. 2. Morphology of batisivite grains, SEM images. The character of fracture is illustrated by images in the lower row.

attracted by the strong faces of a Sochnev magnet, and is insoluble in HCl.

In reflected light, batisivite is almost white, occasionally with a weak cream hue and without internal reflections. At crossed polars, weak anisotropy is observable. The reflectance of batisivite was measured in random (nonoriented) sections of two grains of similar composition. The new mineral is characterized by a weak to moderate bireflectance; the reflectance spectra (recorded in air) have minimums within a range of 480–

500 nm against the overall rise in the long-wave region (Table 1, Fig. 3).

CRYSTALLOGRAPHY

A.A. Kashaev performed the preliminary X-ray single crystal study of batisivite with the Laue, rotation–swinging, and Weissenberg methods and photography of the reciprocal lattice (KFOR camera). Two grains of up to 100–150 μm in size were examined. At the same time, Z.F. Ushchapovskaya carried out X-ray powder

Table 1. Reflectance (R, %) of batisivite

Reflectance		R values for variable wavelengths (nm)													
		440	460	480	500	520	540	560	580	600	620	640	660	680	700
R'_{max}	1	17.40	17.20	17.12	17.24	17.42	17.49	17.54	17.60	17.69	17.72	17.78	17.85	17.95	18.10
	2	17.61	17.36	17.10	17.08	17.21	17.30	17.41	17.52	17.61	17.71	17.81	17.86	17.94	18.09
R'_{min}	1	16.92	16.68	16.56	16.59	16.70	16.80	16.82	16.93	17.01	17.06	17.15	17.23	17.35	17.44
	2	17.10	16.72	16.52	16.58	16.69	16.77	16.82	16.88	16.98	17.04	17.10	17.16	17.22	17.34

Note: R values were measured on a MSF-10 microspectrophotometer; slit of monochromator is 0.4 mm (degree of monochromaticity is 12–15 nm), beam is 0.03 mm, and metallic Si is the standard.

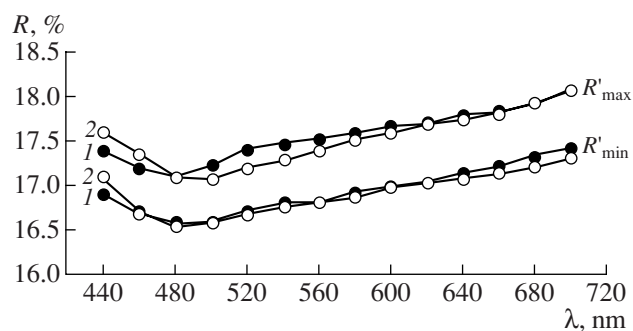


Fig. 3. Reflectance spectra of batisivite. 1 and 2 are grains 1 and 2 in Table 1.

diffraction of the third grain. Due to the small sizes of grains, the Laue patterns are distinguished by weak reflections. Plane of symmetry m was tentatively recorded in one of the patterns; swinging along the normal to the plane allowed determination of the identity period accepted as direction b . Sweeps of the $h0l$ and hll layer lines in the Wiessenberg and KFOR goniometers made it possible to select the monoclinic cell and to index the Debye powder pattern in parameters of single crystal data $a = 7.02$, $b = 14.3$, $c = 5.01$ Å, $\beta = 104^\circ$ and diffraction symmetry group $A2/m$ by observed extinctions $k + l \neq 2n$. These data are close to the characteristics of barian tomichite, a known mineral from the derbylite group (Grey et al., 1987). It should be noted that some reflections in the X-ray single crystal diffraction patterns were not indexed, indicating an admixture or different symmetry of crystal.

To obtain the unambiguous results, T. Armbruster analyzed another grain by an Enraf Nonius CAD 4 single crystal automatic diffractometer. The complete structural data on the batisivite structure obtained from the single crystal study will be reported in a separate paper (Armbruster et al., in press). A brief description of the mineral structure is presented in this paper.

According to the strong reflections, the X-ray diffraction pattern was attributed to the C -centered monoclinic unit cell with parameters corresponding to derbylite group minerals; i.e., as a rough approximation, the preliminary results have been confirmed. However, there were a number of additional weak reflections with halfwidths larger than that of reflections of the monoclinic sublattice. Taking into account all reflections, the X-ray diffraction data were indexed in the triclinic unit cell with the following dimensions: $a = 7.5208(4)$, $b = 7.6430(4)$, $c = 9.5724(4)$ Å; $\alpha = 110.204(3)^\circ$, $\beta = 103.338(6)^\circ$, $\gamma = 98.281(7)^\circ$; $V = 487.14(7)$ Å³; space group $P\bar{1}$; $Z = 1$.

Similar to other minerals of the derbylite group, including derbylite, barian tomichite, Pb-bearing graeserite, etc. (Moore and Araki, 1976; Grey et al., 1987; Berlepsch and Armbruster, 1998), the lattice of batisivite is a combination of zigzag double chains of

octahedrons of α - PbO_2 -type structure (sites $M1$ – $M4$) and columns of V_2O_5 -type structure ($M5$ – $M8$). The channels formed by a combination of these structure units can be described as chains of cuboctahedral cavities running parallel to $[011]$ in a triclinic system. Ti, V, Cr, Fe, and Nb occupy the octahedral sites of batisivite, while alternating barium and silicon–oxygen groups occupy cuboctahedral sites. The latter can be regarded with equal probability as diorthogroup Si_2O_7 or quasi-molecule Si_2O (Handke and Mozgawa, 1995). In the first case, the ideal formula of batisivite is $M_{14}[Ba(Si_2O_7)](O,OH)_{22}$, and $M_{14}[Ba(Si_2O)](O,OH)_{28}$ in the second case. The latter variant makes it possible to retain the crystallochemical formula that fits the structure type of the derbylite group of minerals and is therefore preferable. The character of the Ba– Si_2O ordering in cuboctahedrons determines the lowering of batisivite symmetry down to the triclinic system. In the structural framework of batisivite formed by octahedrons, two positions of oxygen (O6, O11) can be potential sites of OH groups. However, in the ideal formula $V_8^{3+}Ti_6^{4+}[Ba(Si_2O)]O_{28}$, oxygens O6 and O11 are additionally bound with Si and Ba, and the hydration of these sites is ruled out.

According to the results of X-ray single crystal study, the line indices of the previous Debye powder pattern was corrected and the unit-cell dimensions were calculated (Table 2). The exceeding errors in the difference of some parameters from the X-ray single crystal study and calculation of the Debye powder pattern are apparently related to significant distinctions between the examined grains in the content of TiO_2 , the (V, Cr, Fe)/Ti ratio, and the calculated V^{4+} content (see below, Table 3).

CHEMICAL COMPOSITION

Batisivite with Ti, V, Cr, Ba, and Si as the major components is a difficult object to examine by electron microprobe due to the distortion of analytical signals from interference by the characteristic lines of Ba and Ti, and cascade superposition of Ti onto V, and V onto Cr. To obtain more reliable data on the chemical composition of the new mineral, it was analyzed using several devices using different techniques in order to take into account or to remove the superpositions (mainly in the same preparations).

Analyses were carried out by N.S. Karmanov and S.V. Kanakin at the Geological Institute, Siberian Branch, Russian Academy of Sciences, on an advanced MAR-3 electron microprobe operating at 20 kV and 40 nA, with a 2- μ m beam diameter. The following standards were used: quartz (Si), rutile (Ti), corundum (Al), chromite (Cr), hematite (Fe), diopside (Mg), barite (Ba), pyrochlore (Nb), and V_2O_5 (V).

E.V. Galuskin and P. Dzerzhanovsky from Warsaw University, Poland, used a CAMECA SX-100 electron

Table 2. X-ray powder diffraction pattern of batisivite

<i>I</i>	<i>d</i> _{meas} (Å)	<i>d</i> _{calc} (Å)	<i>hkl</i>	<i>I</i>	<i>d</i> _{meas} (Å)	<i>d</i> _{calc} (Å)	<i>hkl</i>
4	3.38	3.38	111	8	1.781	1.785	32 $\bar{4}$
8 br	3.10	3.09	12 $\bar{2}$	10	1.582	1.581	24 $\bar{2}$
10	2.85	2.84, 2.85	021, 120	2 dif	1.497	1.495	33 $\bar{5}$
8	2.63	2.64	21 $\bar{3}$	10 br	1.433	1.432, 1.433	322, 124
4	2.48	2.48, 2.47	03 $\bar{2}$	2	1.394	1.393	50 $\bar{4}$
6	2.23	2.23	220	2	1.356	1.356	24 $\bar{6}$
8	2.13	2.12	31 $\bar{3}$	4	1.068	1.068	45 $\bar{2}$
2	2.03	2.03, 2.04	113, 031	6	1.034	1.034	51 $\bar{8}$
2	1.872	1.873	311				

Unit-cell dimensions
 $a = 7.53(1) \text{ \AA}$ $b = 7.62(1) \text{ \AA}$ $c = 9.58(1) \text{ \AA}$
 $\alpha = 110.36^\circ(4)$ $\beta = 103.28^\circ(4)$ $\gamma = 98.15^\circ(5)$
 $V = 486.7(5) \text{ \AA}^3$

Note: RKD-57.3 camera; the sample is a rubber bowl 0.3 mm in diameter; asymmetric film loading; FeK α irradiation. Because of small volume of sample, it was analyzed without standard. Analyst, Z.F. Ushchapovskaya.

microprobe operating at 15 kV and 20 nA, with a 1–2- μm beam diameter. The following standards were used: LiNbO₃ (Nb), diopside (Mg, Si), orthoclase (Al), TiO₂ (Ti), BaSO₄ (Ba), Cr₂O₃ (Cr), Fe₂O₃ (Fe), and pure metallic V (V).

A Superprobe-733 Jeol (JCSA-733) electron microprobe operating at 15 kV and 20 nA, with a 2- μm beam diameter was used by L.F. Suvorova at the Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences. The following standards were used: ilmenite GF-51 (Ti), chromite UV-26 and Cr-spinel (Cr, Fe, Al), barite (Ba), diopside (Si, Mg), and V₂O₅ (V).

M.D. Tolkachev and M.R. Pavlov performed analyses at the Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, on an ABT-55 scanning electron microscope equipped with a Link AN-1000/S85 EDS. The following standards were used: pure metals (Ti, V, Cr, Fe), SiO₂ (Si), MgO (Mg), Al₂O₃ (Al), and BaF₂ (Ba).

In total, 237 point analyses of 72 grains were conducted; about 80% of the analyses were carried out on MAR-3 and CAMECA SX-100 electron microprobes. Comparison of the results has shown appreciable discrepancies in the average or predominant sums and contents of the major components TiO₂—(Cr₂O₃ + V₂O₃) and their relationships between series of analyses performed in different laboratories and with different equipments. At the same time, similar discrepancies were established between duplicate series of samples analyzed in different periods at the same laboratory. Probably even little changes in equipment calibration affect the analytical results. Nevertheless, the available

dataset allows correct estimation of the chemical composition of batisivite.

Substantial variations both in major (TiO₂, V₂O₃, Cr₂O₃, SiO₂) and minor (Fe₂O₃, Al₂O₃, Nb₂O₅) components are characteristic of this mineral. The stable BaO contents are the only exception. Variations of concentrations within individual grains are noticeably less than those between different grains even from the same sample. It should be noted that similar compositional variability at the macro- and microscopic levels is characteristic of almost all chromium–vanadium and Cr–V-bearing minerals from the host metamorphic rocks, including pyroxenes, amphiboles, micas, garnets, simple and complex oxides, etc. (Konev et al., 2001), and metamorphic minerals of chromium and vanadium as a whole. With the exception of BaO, all components of batisivite correlate with one another at different confidence levels. The strongest negative correlation is between Ti and the sum of (V + Cr + Fe) at an octahedral site (Fig. 4a) and between the leading components Ti–V and V–Cr. Representative analyses and average chemical compositions of individual grains illustrating a broad range of Ti/V ratio and variations of other components, as well as average, medium, and maximum concentrations in the entire dataset are given in Table 3.

In addition to batisivite, the derbylite group includes tomichite and its barian variety, graeserite and Pb-bearing graeserite, and hemloite. Except for hemloite, the minerals of this group have the structural formula $M_7TO_{13}(\text{OH})$ at $Z = 2$ or $M_{14}T_2O_{26}(\text{OH})_2$ per unit cell, where M represents octahedral sites, and T , the cuboctahedral sites in channels. In the structure of batisivite,

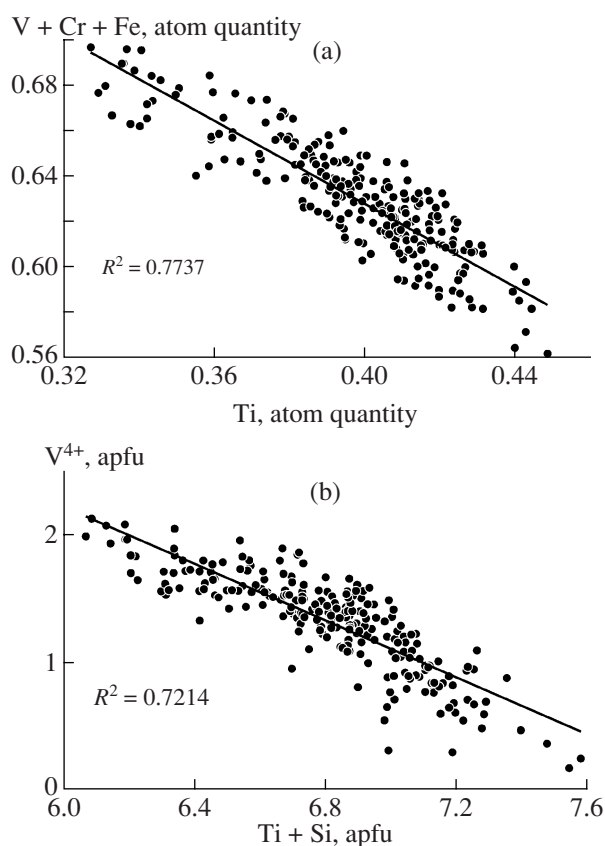


Fig. 4. Cation ratios in batisivite: (a) (V + Cr + Fe) versus Ti in atom quantities and (b) V^{4+} versus (Ti + Si), apfu.

barium and silicon occupy cuboctahedrons and substitution of Ba for 2Si is accompanied by additional bridge oxygen in cuboctahedrons. Therefore, an amount of oxygen in batisivite is not fixed, and the idealized sum of cations can be between 16 and 18. The stable sum of cations (V, Cr, Fe, Nb) in the octahedral framework is accepted as 14; this sum serves as the basis for calculation. According to structural data, the presence of the OH group in batisivite is unlikely, and this is confirmed by the results of Raman spectroscopy. Due to the absence of OH, the most reliable version of charge compensation at heterovalent isomorphic substitutions $R^{3+} \rightarrow Ti^{4+}$ and $Al \rightarrow Si$ (in cuboctahedrons) is a partial transition of V^{3+} to V^{4+} . To calculate V^{4+} , the amount of oxygen was accepted as 28 (the standard value of the derbylite group) plus $(Si + Al)/2$ as an additional bridge oxygen in cuboctahedrons. The estimation of the percentage of $V^{4+}(VO_2)$ strongly depends on the accuracy at which all components are determined and, taking into account the complexity of analysis, should be considered approximate. As a rule, the amount of V^{4+} is larger than necessary for the compensation of Ti deficiency and substitution of Al for Si. At the same time, the strong negative correlation between (Ti + Si) and calculated V^{4+} (Fig. 4b) testifies in favor of the proposed approach.

Theoretically, R^{3+} and R^{4+} (Ti, V, Cr, Fe) and Nb can occupy all octahedral sites $M1-M8$ in the structure of batisivite. However, if relatively large sizes of $M1-M4$ are taken into account, they must preferably be occupied by larger R^{3+} cations and Nb, while positions $M5-M8$, by Ti and a part of V^{4+} that have relatively small apparent ion radii. In this case, the empirical formula of batisivite can be expressed as $(V_{4.77}^{3+}V_{0.75}^{4+}Cr_{2.20}Fe_{0.25}Nb_{0.03})_{8.0}(Ti_{5.41}V_{0.59}^{4+})_{6.0}[Ba_{1.01}Mg_{0.02}(Si_{1.40}Al_{0.48}O_{0.94})]O_{28}$. The ideal formula is $V_8Ti_6[Ba(Si_2O)]O_{28}$; theoretical chemical composition calculated from this formula is as follows (wt %): 44.33 V_2O_3 , 35.45 TiO_2 , 8.88 SiO_2 , 11.34 BaO. The alternative version of the ideal formula (with diorthogroup) is $V_8Ti_6[Ba(Si_2O_7)]O_{22}$. As was mentioned above, we give preference to the first version.

Despite the significant content of Cr_2O_3 , Cr is not included in the ideal formula of batisivite, because a wide range of isomorphic substitution V for Cr up to the formation of end members is characteristic of most chromium–vanadium minerals in the Sludyanka Complex including minerals associated with batisivite. In particular, these series have been established for clinopyroxenes (kosmochlor–nataliite), tourmalines (chromdravite–vanadiumdravite), garnets (uvarovite–goldmanite), simple oxides (escolaite–karelianite), and spinels (magnesiocromite–magnesiocoulsonite) (Konev et al., 2001). Therefore, the formation of a Cr analogue of batisivite (at a larger Cr/V ratio in the bulk rock composition) and Cr and V end members of the $V_8^{3+}Ti_6^{4+}[Ba(Si_2O)]O_{28}-Cr_8^{3+}Ti_6^{4+}[Ba(Si_2O)]O_{28}$ series may be suggested.

DISCUSSION

Among the known minerals of the derbylite group, batisivite is distinguished by the absence of hydroxyl and the occurrence of V as V^{3+} and V^{4+} species. Although the presence of V^{4+} has not been proven by direct methods, there are sufficient reasons to accept its possibility. A number of Ti–V(Cr) oxides are associated with batisivite, and comparison of chemical composition and X-ray structural data in each of these minerals indicates the reality of isomorphic substitution of $V^{4+} \leftrightarrow Ti$. In schreyerite $V_2Ti_3O_9$, for which an X-ray single crystal study was performed for the first time, the $R^{3+}(V, Cr, Fe)/Ti$ ratio exceeds 2/3, and the charge balance is reached only at a variable valence of vanadium with about 1/4–1/5 of V as V^{4+} species (Döbellin et al., 2006). A similar situation is characteristic of ankangite and berdesinskiite. Among unnamed minerals, there is an oxide of V_3O_5 type forming the $V_2^{3+}V^{4+}O_5-V_2^{3+}TiO_5$ solid solution series, where the isomorphic substitution Ti^{4+} for V^{4+} is widely developed. Previously, such isomorphic substitution was established in zoltaiite (Bartholomew et al., 2005). We should suppose that Ti–V-bearing

Table 3. Chemical composition of batisivite, wt %

Component	1	2	3	4	5	6	7	8	9	10	11	12	13
Nb ₂ O ₅	0.00	n.a.	n.a.	0.31	0.30	0.81	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.24
SiO ₂	5.66	5.55	5.43	5.45	6.20	6.03	6.36	5.78	5.38	6.35	6.56	7.09	6.69
TiO ₂	35.37	35.09	34.43	34.26	33.51	33.05	32.82	32.63	32.45	32.17	31.83	31.67	31.38
Al ₂ O ₃	2.16	2.30	2.51	2.19	1.91	2.14	1.69	2.06	1.69	1.62	1.46	1.73	1.59
V ₂ O ₃ *	28.02	25.50	29.63	29.15	32.44	28.39	32.03	34.26	31.37	33.33	33.13	33.38	36.56
Cr ₂ O ₃	14.95	17.09	15.39	14.03	12.09	17.12	10.14	10.42	12.56	12.31	13.07	13.31	9.90
Fe ₂ O ₃	1.87	1.96	0.97	2.51	1.51	0.46	5.06	2.00	3.46	1.95	1.75	1.07	2.10
MgO	0.11	0.07	0.09	0.10	0.06	0.11	0.08	0.09	0.14	0.08	0.00	0.30	0.11
BaO	11.55	11.32	11.29	11.32	11.78	11.36	11.28	11.47	11.40	10.98	11.31	11.45	11.51
Total	99.69	98.88	99.74	99.32	99.80	99.47	99.46	98.71	98.45	98.79	99.41	100.00	100.08
VO ₂ **	5.85	5.92	7.33	7.68	5.60	5.43	7.41	7.91	11.34	8.62	8.62	4.02	7.56
V ₂ O ₃ **	22.74	20.15	23.01	22.21	27.38	23.48	25.33	27.11	21.13	25.54	25.34	29.75	29.72
Total	100.26	99.45	100.44	100.06	100.34	99.97	100.16	99.48	99.55	99.61	99.96	100.39	100.78
Coefficients in formula calculated on the basis of 14 cations (Ti + Cr + V + Fe + Nb)													
Si	1.273	1.257	1.216	1.225	1.399	1.364	1.431	1.311	1.213	1.430	1.477	1.602	1.500
Al	0.572	0.613	0.663	0.580	0.508	0.571	0.448	0.551	0.450	0.429	0.387	0.460	0.419
Ti	5.978	5.976	5.796	5.795	5.687	5.625	5.557	5.564	5.503	5.453	5.392	5.386	5.292
V ⁴⁺	0.952	0.971	1.189	1.251	0.916	0.890	1.208	1.299	1.852	1.408	1.407	0.658	1.229
V ³⁺	4.098	3.658	4.130	4.004	4.954	4.261	4.573	4.928	3.820	4.615	4.577	5.395	5.345
Cr	2.656	3.060	2.723	2.494	2.157	3.063	1.805	1.867	2.238	2.194	2.327	2.380	1.756
Fe	0.316	0.335	0.163	0.425	0.256	0.079	0.857	0.342	0.587	0.331	0.297	0.182	0.354
Nb	–	–	–	0.031	0.031	0.082	–	–	–	–	–	–	0.024
Mg	0.036	0.024	0.031	0.032	0.020	0.036	0.028	0.032	0.046	0.026	–	0.100	0.035
Ba	1.017	1.004	0.990	0.998	1.041	1.007	0.995	1.019	1.007	0.969	0.998	1.014	1.012
Total	16.898	16.898	16.901	16.835	16.969	16.978	16.902	16.913	16.716	16.855	16.862	17.177	16.966

Table 3. (Contd.)

Component	14	15	16	17	18	19	20	21	22	23	24
Nb ₂ O ₅	n.a.	n.a.	n.a.	0.25	0.23	0.21	n.a.	n.a.	0.34	0.31	0.26(0.00–0.99)
SiO ₂	8.17	5.95	6.19	5.96	6.34	6.23	6.76	6.82	6.76	7.03	6.16(5.38–8.17)
TiO ₂	31.23	30.67	30.43	30.35	29.67	29.15	28.74	27.44	26.91	26.15	31.76(26.15–35.82)
Al ₂ O ₃	1.43	1.80	1.56	2.10	1.51	1.82	1.50	1.38	1.23	1.15	1.81(0.97–2.51)
V ₂ O ₃ *	34.08	37.49	36.72	36.12	38.08	40.50	38.92	41.23	42.34	42.32	33.68(23.03–42.34)
Cr ₂ O ₃	12.11	10.49	12.05	12.46	10.50	8.02	10.13	9.54	9.28	9.12	12.29(7.13–20.49)
Fe ₂ O ₃	1.71	0.88	0.38	0.78	1.49	0.76	1.94	0.67	0.69	0.76	1.48(0.33–5.18)
MgO	0.11	0.13	0.00	0.09	0.08	0.03	0.12	0.09	0.11	0.02	0.08(0.00–0.66)
BaO	11.04	11.27	11.32	11.20	11.40	11.93	11.28	11.51	11.30	11.42	11.42(10.39–12.25)
Total	99.88	98.68	98.65	99.31	99.30	98.65	99.39	98.68	98.96	98.28	98.94(96.31–101.78)
VO ₂ **	1.84	10.64	11.25	10.21	11.13	9.49	10.59	11.19	12.84	12.10	8.20(1.07–13.05)
V ₂ O ₃ **	32.41	27.88	26.56	26.89	28.58	31.93	29.35	31.12	30.74	31.39	26.97(16.99–34.63)
Total	100.05	99.71	99.73	100.28	100.93	99.58	100.40	99.75	100.20	99.45	99.73(97.13–102.11)
Coefficients in formula calculated on the basis of 14 cations (Ti + Cr + V + Fe + Nb)											
Si	1.856	1.342	1.394	1.340	1.423	1.421	1.519	1.546	1.522	1.600	1.394(1.213–1.856)
Al	0.382	0.477	0.414	0.555	0.399	0.489	0.396	0.369	0.326	0.308	0.483(0.261–0.663)
Ti	5.331	5.201	5.156	5.126	5.008	4.998	4.858	4.679	4.555	4.475	5.408(4.475–6.209)
V ⁴⁺	0.303	1.738	1.836	1.661	1.822	1.567	1.724	1.838	2.093	1.995	1.345(0.179–2.133)
V ³⁺	5.900	5.041	4.798	4.843	5.031	5.837	5.289	5.658	5.547	5.727	4.769(3.092–6.314)
Cr	2.174	1.870	2.146	2.213	1.864	1.446	1.800	1.710	1.652	1.641	2.200(1.251–3.678)
Fe	0.292	0.150	0.064	0.132	0.252	0.130	0.328	0.114	0.117	0.130	0.252(0.057–0.870)
Nb	–	–	–	0.025	0.023	0.022	–	–	0.035	0.032	0.027(0.000–0.103)
Mg	0.036	0.045	–	0.031	0.027	0.010	0.040	0.030	0.035	0.007	0.027(0.000–0.224)
Ba	0.982	0.996	0.999	0.985	1.002	1.066	0.993	1.023	0.997	1.018	1.014(0.907–1.085)
Total	17.256	16.860	16.807	16.911	16.851	16.986	16.947	16.967	16.879	16.933	16.918(16.705–17.350)

Note: (1–23) are representative particular analyses and compositions of individual grains; (24) is the average composition; the range of contents in parentheses; n.a. stands for not analyzed. The X-ray single crystal study was performed for grain 5; the powder pattern was recorded for grain 18; the reflectance spectra were obtained for grain 12 and a similar grain.

* V₂O₃tot.

** Calculated values, all Fe as Fe₂O₃.

oxides readily react to redox conditions of mineral deposition and may be regarded as potential geological oxybarometers.

The origin of Cr–V-bearing metamorphic rocks and assemblages of Cr and V minerals in the rocks was repeatedly discussed, in particular, in the description of vanadiumdravite (Reznitsky et al., 2001) and by (Konev et al., 2001). The rocks of the Slyudyanka Complex metamorphosed under granulite-facies conditions and were affected by high- and medium-temperature retrograde metamorphism. Chromium–vanadium and Cr–V-bearing minerals were formed at the prograde and retrograde metamorphic stages. Granulite-facies metamorphism is usually characterized by relatively reduced conditions. Since batisivite and associated Ti–V oxide minerals are distinguished by an elevated degree of vanadium oxidation, they are most likely deposited during retrograde stages at relatively low temperatures and high oxygen fugacity.

The type material of batisivite has been deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no 06-05-64300).

REFERENCES

1. T. Armbruster, L. Z. Reznitsky, E. V. Sklyarov, and E. V. Galuskin, "The Crystal Structure of Batisivite: A New Mineral from Derbylite Group" (in press).
2. P. R. Bartholomew, F. Mancini, Ch. Cahill, et al., "Zoltaiite, a New Barium-Vanadium Nesosubsilicate Mineral from British Columbia: Description and Crystal Structure," *Am. Mineral.* **90** (10), 1655–1660 (2005).
3. P. Berlepsch and T. Armbruster, "The Crystal Structure of Pb²⁺-Bearing Graeserite. Pb_{0.14}(Fe, Ti)₇AsO_{12+x}(OH)_{2-x}, a New Mineral of the Derbylite Group," *Schweiz. Miner. Petr. Mitt.* **78** (1), 1–9 (1998).
4. N. Döbelin, L. Z. Reznitsky, E. V. Sklyarov, et al., "Schreyerite, V₂Ti₃O₉: New Occurrence and Crystal Structure," *Am. Mineral.* **91** (1), 196–202 (2006).
5. I. E. Grey, I. C. Madsen, and D. C. Harris, "Barian Tomichite, Ba_{0.5}(As₂)_{0.5}Ti₂(V, Fe)₅O₁₃(OH), Its Crystal Structure and Relationship to Derbylite and Tomichite," *Am. Mineral.* **72** (1–2), 201–208 (1987).
6. M. Handke and W. Mozgawa, "Model Quasi-Molecule Si₂O as an Approach in the IR Spectra Description Glassy and Crystalline Framework Silicates," *J. Mol. Struct.* **348**, 341–344 (1995).
7. A. A. Konev, L. Z. Reznitsky, G. D. Feoktistov, et al., *Mineralogy of East Siberia on the Turn of XXI Century (New and Rare Minerals)* (Intermet-Engineering, Moscow, 2001) [in Russian].
8. P. B. Moore and T. Araki, "Derbylite, Fe₄³⁺Ti₃⁴⁺Sb³⁺O₁₃(OH), a Novel Close-Packed Oxide Structure," *Neues. Jb. Miner. Abh.* **126** (3), 292–303 (1976).
9. L. Z. Reznitsky, E. V. Sklyarov, Z. F. Ushchapovskaya, et al., "Vanadiumdravite NaMg₃V₆[Si₆O₁₈][VO₃]₃(OH)₄, a New Mineral of Tourmaline Group," *Zap. Vseross. Mineral. O–va* **130** (2), 59–72 (2001).
10. E. P. Vasil'ev, L. Z. Reznitsky, V. N. Vishnyakov, and E. A. Nekrasova, *The Slyudyana Crystalline Complex* (Nauka, Novosibirsk, 1981) [in Russian].