

## Koksharovite, $\text{CaMg}_2\text{Fe}^{3+}_4(\text{VO}_4)_6$ , and grigorievite, $\text{Cu}_3\text{Fe}^{3+}_2\text{Al}_2(\text{VO}_4)_6$ , two new howardevansite-group minerals from volcanic exhalations

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**Abstract:** Two new howardevansite-group minerals were discovered in the exhalations of fumaroles related to two volcanoes in Kamchatka, Russia. Koksharovite,  $\text{CaMg}_2\text{Fe}^{3+}_4(\text{VO}_4)_6$ , is found at the Bezmyannyi volcano in association with bannermanite. Grigorievite,  $\text{Cu}_3\text{Fe}^{3+}_2\text{Al}_2(\text{VO}_4)_6$ , associated with bannermanite, ziesite, hematite, *etc.*, was found at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano. Koksharovite occurs as equant to prismatic crystals up to  $30 \times 70 \mu\text{m}$ . It is translucent, yellowish-brown to reddish-brown with an adamantine lustre. Grigorievite forms prismatic to tabular crystals up to  $40 \times 100 \mu\text{m}$ . It is opaque, black with a semi-metallic lustre. Both minerals are brittle. The VHN hardness is 368 and 489  $\text{kg mm}^{-2}$ , the calculated density ( $D_{\text{calc}}$ ) 3.39 and 3.67  $\text{g cm}^{-3}$  for koksharovite and grigorievite, respectively. In reflected light, koksharovite is light grey, grigorievite is grey; both minerals are weakly anisotropic. Reflectance values [koksharovite//grigorievite:  $R_{\text{max}}-R_{\text{min}}$ , % ( $\lambda$ , nm)] are: 15.3–14.4//16.8–16.4 (470), 14.1–13.2//15.9–15.5 (546), 13.8–13.0//15.3–14.9 (589), 13.4–12.7//14.8–14.1 (650). Chemical data (wt%, electron-microprobe analysis; first value is for koksharovite, second for grigorievite) are:  $\text{Na}_2\text{O}$  0.76, 0.00;  $\text{K}_2\text{O}$  0.05, 0.00;  $\text{MgO}$  9.43, 2.78;  $\text{CaO}$  3.57, 0.95;  $\text{MnO}$  0.46, 0.04;  $\text{CuO}$  0.00, 17.70;  $\text{NiO}$  0.11, 0.00;  $\text{ZnO}$  0.00, 0.14;  $\text{Al}_2\text{O}_3$  3.04, 11.76;  $\text{Fe}_2\text{O}_3$  23.88, 10.10;  $\text{TiO}_2$  2.42, 1.47;  $\text{SiO}_2$  0.20, 0.00;  $\text{P}_2\text{O}_5$  0.98, 0.13;  $\text{V}_2\text{O}_5$  53.86, 54.97; total 98.76, 100.04. The empirical formulae, based on 24 O atoms per formula unit, are:  $\text{Na}_{0.24}\text{K}_{0.01}\text{Ca}_{0.63}\text{Mg}_{2.30}\text{Mn}_{0.06}\text{Ni}_{0.01}\text{Al}_{0.59}\text{Fe}^{3+}_{2.94}\text{Ti}_{0.30}\text{Si}_{0.03}\text{P}_{0.14}\text{V}_{5.83}\text{O}_{24}$  (koksharovite);  $\text{Ca}_{0.17}\text{Mg}_{0.69}\text{Mn}_{0.01}\text{Cu}_{2.23}\text{Zn}_{0.02}\text{Al}_{2.31}\text{Fe}^{3+}_{1.27}\text{Ti}_{0.18}\text{P}_{0.02}\text{V}_{6.05}\text{O}_{24}$  (grigorievite). Both minerals are triclinic, space group  $P-1$ ,  $Z = 1$ . Unit-cell dimensions are:  $a$  8.1758(7),  $b$  9.8292(9),  $c$  6.6940(6) Å,  $\alpha$  105.041(8),  $\beta$  102.040(8),  $\gamma$  106.025(8)°,  $V$  476.02(8) Å<sup>3</sup> for koksharovite;  $a$  8.0217(5),  $b$  9.6858(10),  $c$  6.5475(9) Å,  $\alpha$  103.645(10),  $\beta$  102.369(8),  $\gamma$  106.281(8)°,  $V$  452.60(8) Å<sup>3</sup> for grigorievite. The strongest reflections of the X-ray powder patterns [ $d$ , Å( $I$ )( $hkl$ )] are: 7.47(28)(100), 3.75(44)(200,  $-201$ ), 3.26(27)(0–12), 3.17(100)(–130), 3.09(94)(–221, 210), 2.039(28)(–3–21,  $-340$ ) for koksharovite; 7.36(24)(100), 4.718(29)(–1–11,  $-111$ ), 3.671(26)(200,  $-201$ ), 3.141(100)(–130), 3.044(92)(210), 2.811(26)(–1–22) for grigorievite. The crystal structure of both minerals [single-crystal X-ray diffraction data,  $R = 0.079$  (koksharovite) and 0.055 (grigorievite)] is based on the pseudo-frameworks built by  $\text{VO}_4$  tetrahedra,  $\text{MIO}_6$  octahedra [species-defining  $\text{MI} = \text{Fe}^{3+}$ , Al] and  $\text{MIO}_5$  polyhedra [ $\text{MII} = (\text{Cu}, \text{Mg})$  in grigorievite and (Mg, Fe) in koksharovite]. The Ca (koksharovite) and Cu(2) sites (grigorievite) are located in tunnels. The new minerals (IMA 2012–092 and 2012–047, respectively) are named in honour of outstanding Russian mineralogists, Nikolay Ivanovich Koksharov (1818–1892) and Dmitry Pavlovich Grigoriev (1909–2003).

**Key-words:** koksharovite; grigorievite; new mineral; crystal structure; howardevansite group; vanadate; fumarole sublimate; Bezmyannyi volcano; Tolbachik volcano; Kamchatka.

### Introduction

Hydrogen-free minerals with pentavalent vanadium are diverse in sublimates of some volcanic fumaroles characterized by oxidizing conditions. Twelve copper vanadates were discovered in fumaroles at two active volcanoes, Izalco (El Salvador) and Tolbachik (Kamchatka peninsula, Far-Eastern Region, Russia);

two oxides with species-defining  $\text{V}^{5+}$  (shcherbinaite and bannermanite) are known at the same volcanoes and at the Bezmyannyi volcano (Kamchatka), and schäferite, the only copper-free vanadate earlier known in this formation, was discovered in paleo-fumarole deposits related to the Quaternary volcanism of Eifel, Germany, and recently found by us at Tolbachik (see Pekov *et al.*, 2013a, for a review)

Table 1. Comparative crystal-chemical data of howardevansite-group minerals.

Mineral	Howardevansite	Koksharovite	Grigorievite
Formula	$\text{Na}_2\text{Cu}_2\text{Fe}^{3+}_4(\text{VO}_4)_6$	$\text{CaMg}_2\text{Fe}^{3+}_4(\text{VO}_4)_6$	$\text{Cu}_3\text{Fe}^{3+}_2\text{Al}_2(\text{VO}_4)_6$
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
Unit-cell data*			
<i>a</i> , Å	8.198	8.1758(7)	8.0217(5)
<i>b</i> , Å	9.773	9.8292(9)	9.6858(10)
<i>c</i> , Å	6.651	6.6940(6)	6.5475(9)
$\alpha$ , °	103.82	105.041(8)	103.645(10)
$\beta$ , °	101.99	102.040(8)	102.369(8)
$\gamma$ , °	106.74	106.025(8)	106.281(8)
<i>V</i> , Å <sup>3</sup>	473	476.02(8)	452.60(8)
<i>Z</i>	1	1	1
Structural formula of the end-member**	$\text{NaNa}\{\text{Cu}_2\text{Fe}^{3+}_2\text{Fe}^{3+}_2(\text{VO}_4)_6\}$	$\text{Ca}\{\text{Mg}_2\text{Fe}^{3+}_2\text{Fe}^{3+}_2(\text{VO}_4)_6\}$	$\text{Cu}\{\text{Cu}_2\text{Fe}^{3+}_2\text{Al}_2(\text{VO}_4)_6\}$
Density (calc.), g cm <sup>-3</sup>	3.81	3.39	3.67
Source	Hughes <i>et al.</i> (1988)	this work	this work

\*Single-crystal data; \*\*the composition of a pseudo-framework built by  $\text{VO}_4$  tetrahedra,  $\text{MIO}_6$  octahedra ( $\text{MI} = \text{Fe}^{3+}$ , Al) and five-fold  $\text{MIIIO}_5$  polyhedra ( $\text{MII} = \text{Cu}$ , Mg) is given in braces.

In this paper we describe two new vanadate minerals found in exhalations of fumaroles related to two active volcanoes at Kamchatka. These minerals are closely related to one another and to howardevansite,  $\text{Na}_2\text{Cu}_2\text{Fe}^{3+}_4(\text{VO}_4)_6$  (Hughes *et al.*, 1988), in terms of crystallographic characteristics and crystal structure. We suggest to unite them as the howardevansite group (Table 1).

The names of both minerals are given in honour of outstanding Russian mineralogists. *Koksharovite*<sup>1</sup> (Cyrillic: кокшаровит) is named after Professor Nikolay Ivanovich Koksharov (1818–1892), Academician of the Russian Academy of Sciences from 1855 and Director of the Russian Mineralogical Society from 1865. Professor Koksharov made the first systematic, extended study of the mineralogy of Russia. His fundamental work *Materials for Mineralogy of Russia* was published in eleven volumes from 1853 to 1892 in Russian and German. He is also well-known as an author for excellent goniometric measurements of crystals of many minerals that are still valid. *Grigorievite* (Cyrillic: григорьевит) is named after Professor Dmitry Pavlovich Grigoriev (1909–2003) who worked at the Saint Petersburg Mining Institute. He was a founder of the ontogenesis of minerals as a specific branch of mineralogy, a specialist in general and theoretical aspects of mineralogy, in the synthesis of analogues of minerals, in extraterrestrial mineralogy and in the teaching of mineralogy.

Both new minerals and their names have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (grigorievite, IMA

2012–047; koksharovite, IMA 2012–092). The type specimens are deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow; the catalogue numbers are 94123 (grigorievite) and 94125 (koksharovite).

## Occurrence and general appearance

Specimens containing both minerals were collected in 1985 by one of the authors (PMK).

Koksharovite is found in a single specimen from the Bezmyannyi (another spelling: Bezmyanny) volcano (55°58'N 160°36'E). The mineral forms equant to prismatic crystals, typically skeletal, up to 30 × 70 μm (usually from 5 to 15 μm) in size and their groups on the surface of andesite scoria (Fig. 1). It is associated with fibrous bannermanite and tiny crystals of two uncharacterized phases, Fe-Al and Ca vanadates. Koksharovite was also found as aggregates up to 80 μm across in the products of alteration of porous scoria by fumarolic gas. A typical example is shown in Fig. 2: koksharovite, biotite, quartz, and (Ti,V)-rich magnetite form complex pseudomorphs after an unknown mineral in altered porous scoria significantly replaced by bannermanite.

Grigorievite is found in specimens collected at the apical part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption (55°41'N 160°14'E). This cone, which is 300 m high and about 0.1 km<sup>3</sup> in volume, is a monogenetic volcano formed in 1975 and located 18 km SSW of the Ploskiy Tolbachik volcano (Fedotov & Markhinin, 1983). Grigorievite forms prismatic to thick tabular crystals (Fig. 3) up to 40 × 100 μm (typically less than 50 μm) in size and their groups associated with hematite on the surface of basalt

<sup>1</sup> A variety of amphibole was once named after N.I. Koksharov. This name was introduced for a hornblende-like mineral in 1857 by N. Nordenskiöld as *kokscharowit* and later (1892) anglicised by E.S. Dana as *koksharovite* (other used variants of its spelling are *kokscharoffite*, *kokcharovite*). It was subsequently discredited as a species name (Leake, 1978). In fact, the name has not been in use for more than one hundred years.

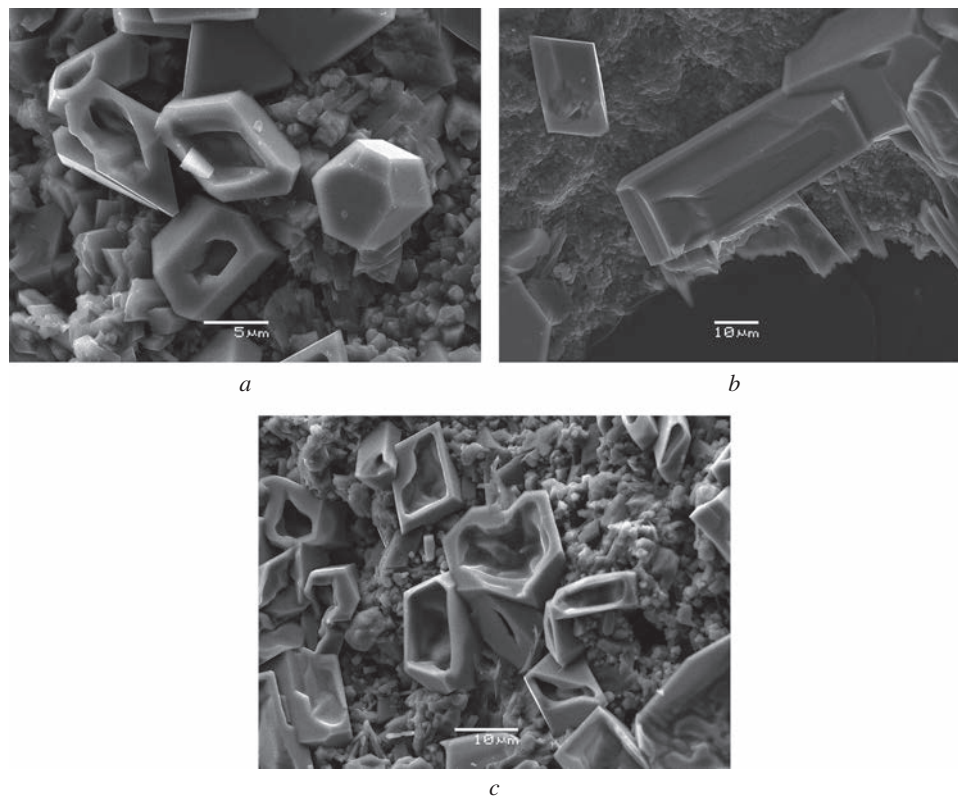


Fig. 1. Crystals of koksharovite. Scanning electron microscope (SEM) images (secondary electrons, SE).

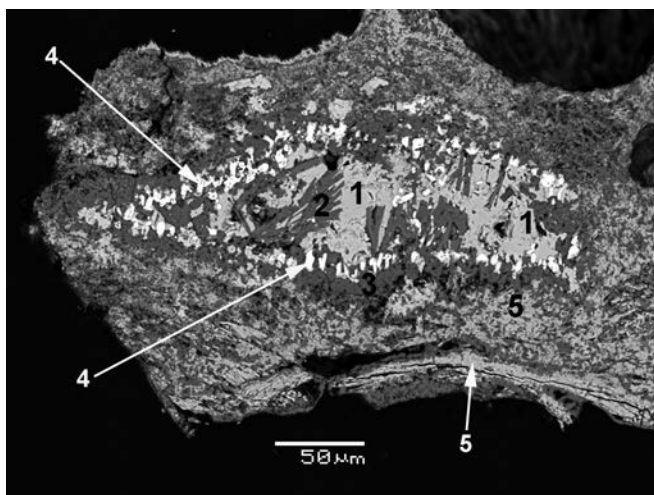


Fig. 2. Pseudomorph consisting of koksharovite (1), biotite (2), quartz (3) and Ti- and V-rich magnetite (4) after an unknown mineral in altered porous andesite scoria significantly replaced by bannermanite (5). Polished section, SEM (back-scattered electrons, BSE) image.

scoria. Bannermanite, Mg-bearing ziesite and two uncharacterized Ca-Cu vanadates overgrow grigorievite (Figs. 3 and 4). Copper sulphates, namely chalcocyanite and euchlorine, crystallized later and form a crust covering

aggregates of the vanadium minerals. The supergene assemblage includes bonattite and chalcantite replacing chalcocyanite exposed to atmospheric air.

We believe that koksharovite, grigorievite and associated vanadium minerals, as well as hematite, chalcocyanite and euchlorine, were deposited directly from the fumarolic gas.

### Physical properties

Koksharovite is translucent, yellowish-brown to reddish-brown with an adamantine luster. The streak is yellowish-brown. The mean micro-indentation hardness (VHN) is 368 with the range 272–458  $\text{kg mm}^{-2}$  (load 20 g). Mohs' hardness was not measured directly because of the tiny size of the available crystals; the value calculated from the VHN is *ca.* 4½.

Grigorievite is opaque, black with a semi-metallic lustre. The streak is reddish-brown. The mean VHN is 489 with the range 412–588  $\text{kg mm}^{-2}$  (load 50 g), which corresponds to a Mohs' hardness of *ca.* 5.

Both minerals are brittle. Cleavage and parting were not observed, and the fracture is uneven (as observed under the scanning electron microscope). Density could not be measured because of the small size and cavernous character of grains of the new minerals. The density calculated using

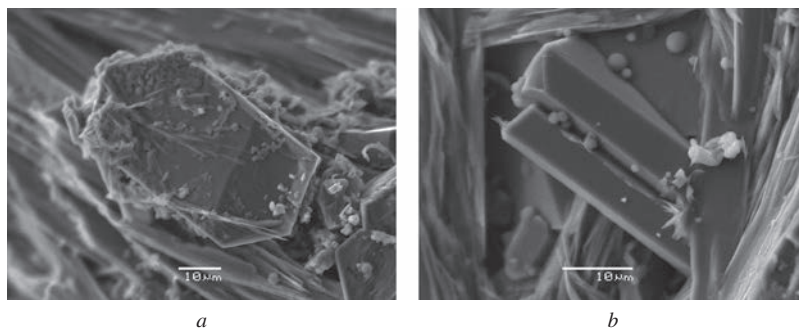


Fig. 3. Grigorievite crystal (a) and parallel intergrowth of crystals (b) with sprays of coarse prismatic crystals of bannermanite. SEM (SE) image.



Fig. 4. Assemblage of vanadium minerals (1–4) on the basalt scoria matrix (5): 1–grigorievite, 2–bannermanite, 3 and 4–epitactic(?), dendritic aggregates of two uncharacterized Ca–Cu vanadates. Polished section, SEM (BSE) image. Field of view: 0.18 mm.

the empirical formulae is 3.39 (koksharovite) and 3.67 (grigorievite)  $\text{g cm}^{-3}$ .

## Optical characteristics

Optical properties of both new minerals were examined in reflected light.

Koksharovite is light grey, and pleochroism was not observed. The bireflectance is weak,  $\Delta R = 0.8\%$  (589 nm). Internal reflections are distinct, yellow-brown to red. Anisotropism is weak.

Grigorievite is grey, non-pleochroic. The bireflectance is weak,  $\Delta R = 0.4\%$  (589 nm). Internal reflections are weak, deep red. Anisotropism is weak.

The reflectance values for both minerals were measured by means of the MSF-21 microspectrophotometer (LOMO, Russia) using the SiC standard (Zeiss, No. 545), they are given in Table 2.

Table 2. Reflectance data ( $R$ , %) for koksharovite and grigorievite.

$\lambda$ , nm	Koksharovite		Grigorievite	
	$R_{\max}$	$R_{\min}$	$R_{\max}$	$R_{\min}$
400	17.5	16.5	17.7	17.3
420	16.9	15.9	17.4	17.0
440	16.2	15.1	17.1	16.8
460	15.6	14.6	16.9	16.5
<b>470</b>	<b>15.3</b>	<b>14.4</b>	<b>16.8</b>	<b>16.4</b>
480	15.1	14.2	16.7	16.3
500	14.8	13.8	16.5	16.1
520	14.4	13.5	16.2	15.9
540	14.1	13.3	16.0	15.6
<b>546</b>	<b>14.1</b>	<b>13.2</b>	<b>15.9</b>	<b>15.5</b>
560	14.0	13.1	15.7	15.4
580	13.8	13.0	15.4	15.0
<b>589</b>	<b>13.8</b>	<b>13.0</b>	<b>15.3</b>	<b>14.9</b>
600	13.7	12.9	15.2	14.8
620	13.5	12.8	15.0	14.5
640	13.4	12.7	14.7	14.2
<b>650</b>	<b>13.4</b>	<b>12.7</b>	<b>14.8</b>	<b>14.1</b>
660	13.3	12.6	14.4	13.9
680	13.2	12.5	14.1	13.7
700	13.2	12.5	13.9	13.5

The values for wavenumbers ( $\lambda$ ) recommended by COM are given in bold type.

## Chemical data

Chemical data for both new minerals were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive (WDS) spectrometer (Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University). The WDS mode was used, with an acceleration voltage of 20 kV, a beam current of 20 nA, and a 2  $\mu\text{m}$  beam diameter. Analytical data are given in Table 3.

The empirical formulae calculated on the basis on 24 O atoms per formula unit (*apfu*) are:

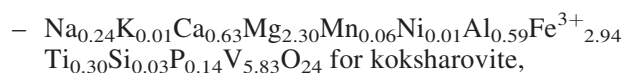


Table 3. Chemical composition (wt%) of koksharovite and grigorievite.

Constituent*	Koksharovite		Grigorievite		Probe standard
	Mean (range) of 3 spot analyses	Ideal <sup>1</sup>	Mean (range) of 5 spot analyses	Ideal <sup>2</sup>	
Na <sub>2</sub> O	0.76 (0.70–0.98)		bdl		NaCl
K <sub>2</sub> O	0.05 (0.03–0.08)		bdl		microcline
MgO	9.43 (8.10–10.83)	8.05	2.78 (2.18–3.22)		olivine
CaO	3.57 (3.05–4.22)	5.60	0.95 (0.90–0.99)		CaWO <sub>4</sub>
MnO	0.46 (0.43–0.52)		0.04 (0.00–0.19)		Mn
CuO	bdl		17.70 (16.75–18.86)	22.82	CuFeS <sub>2</sub>
NiO	0.11 (0.00–0.22)		bdl		Ni
ZnO	bdl		0.14 (0.07–0.24)		ZnS
Al <sub>2</sub> O <sub>3</sub>	3.04 (1.66–5.16)		11.76 (10.03–12.36)	9.75	Al <sub>2</sub> O <sub>3</sub>
Fe <sub>2</sub> O <sub>3</sub> **	23.88 (23.59–24.05)	31.88	10.10 (9.26–11.92)	15.27	CuFeS <sub>2</sub> ; FeAsS
TiO <sub>2</sub>	2.42 (2.00–2.99)		1.47 (1.12–1.65)		ilmenite; TiO <sub>2</sub>
SiO <sub>2</sub>	0.20 (0.13–0.25)		bdl		olivine
P <sub>2</sub> O <sub>5</sub>	0.98 (0.44–1.29)		0.13 (0.00–0.24)		GaP
V <sub>2</sub> O <sub>5</sub>	53.86 (53.19–54.97)	54.47	54.97 (54.34–55.28)	52.16	V; Cu <sub>3</sub> VS <sub>4</sub>
Total	98.76	100.00	100.04	100.00	

1—calculated for the idealized formula CaMg<sub>2</sub>Fe<sup>3+</sup><sub>4</sub>(VO<sub>4</sub>)<sub>6</sub>; 2—calculated for the idealized formula Cu<sub>3</sub>Fe<sup>3+</sup><sub>2</sub>Al<sub>2</sub>(VO<sub>4</sub>)<sub>6</sub>.

\*Contents of other elements with atomic numbers higher than carbon are below detection limits (bdl).

\*\*Fe is considered as Fe<sup>3+</sup> on the basis of the crystal-structure data for both minerals and all structurally related compounds, and of strongly oxidizing conditions associated with mineral deposition in the parent fumaroles (see text).

– Ca<sub>0.17</sub>Mg<sub>0.69</sub>Mn<sub>0.01</sub>Cu<sub>2.23</sub>Zn<sub>0.02</sub>Al<sub>2.31</sub>Fe<sup>3+</sup><sub>1.27</sub>Ti<sub>0.18</sub>  
P<sub>0.02</sub>V<sub>6.05</sub>O<sub>24</sub> for grigorievite.

The simplified formulae and the idealized end-member formulae, respectively, written taking into account the crystal structure data (see below), are:

- koksharovite: (Ca, □)(Mg, Fe<sup>3+</sup>)<sub>2</sub>(Fe<sup>3+</sup>, Mg, Al, Ti)<sub>4</sub>(VO<sub>4</sub>)<sub>6</sub> and CaMg<sub>2</sub>Fe<sup>3+</sup><sub>4</sub>(VO<sub>4</sub>)<sub>6</sub>;
- grigorievite: Cu(Cu, Mg)<sub>2</sub>(Fe<sup>3+</sup>, Al)<sub>2</sub>(Al, Fe<sup>3+</sup>)<sub>2</sub>(VO<sub>4</sub>)<sub>6</sub> and Cu<sub>3</sub>Fe<sup>3+</sup><sub>2</sub>Al<sub>2</sub>(VO<sub>4</sub>)<sub>6</sub>.

## X-ray crystallography

X-ray powder diffraction data for koksharovite (Table 4) and grigorievite (Table 5) were collected using a STOE IPDS II diffractometer equipped with Image Plate area detector, using the Gandolfi method (with MoK $\alpha$  radiation and a detector-to-sample distance of 200 mm). The dimensions of triclinic unit cells refined from the powder data are:

- koksharovite:  $a = 8.16(7)$ ,  $b = 9.83(8)$ ,  $c = 6.70(6)$  Å,  $\alpha = 105.1(3)$ ,  $\beta = 102.0(3)$ ,  $\gamma = 105.8(3)^\circ$  and  $V = 476(3)$  Å<sup>3</sup>;
- grigorievite:  $a = 8.02(6)$ ,  $b = 9.69(8)$ ,  $c = 6.55(5)$  Å,  $\alpha = 103.6(3)$ ,  $\beta = 102.3(3)$ ,  $\gamma = 106.1(3)^\circ$  and  $V = 454(2)$  Å<sup>3</sup>.

Single-crystal X-ray studies for both minerals were carried out using an Xcalibur S diffractometer equipped with a CCD detector. The unit-cell parameters found from single-crystal data are given in Table 1. The data were corrected

for Lorentz and polarization effects. An absorption correction was applied according to the shape of the crystals.

## Howardevansite-group minerals: crystal structures and comparative crystal chemistry

The structure models for koksharovite and grigorievite were obtained by direct methods from single-crystal X-ray diffraction data in the frame of space group *P*-1 and refined to  $R = 0.079$  for koksharovite [1643 independent reflections with  $I > 2\sigma(I)$ ] and to  $R = 0.055$  for grigorievite [1888 independent reflections with  $I > 2\sigma(I)$ ] with the use of SHELX software package (Sheldrick, 2008). All atom sites were refined anisotropically except the low-occupancy Na site in koksharovite. Data-collection information and structure-refinement details for both minerals are given in Table 6. Atom coordinates, displacement parameters and bond-valence sums (parameters for bond valence calculations were taken from Brese & O'Keefe, 1991; the sums were calculated taking into account site occupancies) are presented in Table 7 for koksharovite and in Table 8 for grigorievite. Selected interatomic distances in both structures are given in Table 9. Anisotropic displacement parameters are compiled in Table S1, freely available online as Supplementary Material linked to this article on the GSW website of the journal: <http://eurjmin.geoscienceworld.org/>.

Koksharovite, CaMg<sub>2</sub>Fe<sup>3+</sup><sub>4</sub>(VO<sub>4</sub>)<sub>6</sub>, and grigorievite, Cu<sub>3</sub>Fe<sup>3+</sup><sub>2</sub>Al<sub>2</sub>(VO<sub>4</sub>)<sub>6</sub>, are structurally close to howardevansite, Na<sub>2</sub>Cu<sub>2</sub>Fe<sup>3+</sup><sub>4</sub>(VO<sub>4</sub>)<sub>6</sub> (Hughes *et al.*, 1988). These three minerals can be united to form the howardevansite group. They adopt space group *P*-1 and have close unit-cell parameters (Table 1).

The crystal structures of howardevansite-group minerals (Fig. 5a–c) are based on the pseudo-frameworks built by

Table 4. X-ray powder diffraction data for koksharovite.

$I_{\text{obs}}$	$d_{\text{obs}}, \text{\AA}$	$I_{\text{calc}}^*$	$d_{\text{calc}}, \text{\AA}^{**}$	$hkl$
16	8.89	4	8.893	010
28	7.47	30	7.491	100
13	7.17	12	7.077	-110
6	5.68	1	5.673	-101
20	4.84	17	4.886	-1-11
18	4.68	10	4.687	1-11
15	4.53	5, 11	4.593, 4.447	-120, 020
23	4.02	12	4.010	1-21
44	3.75	19, 17	3.745, 3.741	200, -201
13	3.53	8	3.538	-220
18	3.43	12	3.425	-121
27	3.26	7, 60	3.285, 3.273	111, 0-12
100	3.17	38, 96, 15	3.211, 3.160, 3.139	-102, -130, 021
94	3.09	40, 100	3.091, 3.087	-221, 210
20	2.936	22	2.895	-1-22
25	2.802	11, 14, 11	2.837, 2.808, 2.777	-202, 1-12, 1-22
18	2.668	8, 4, 9, 14	2.695, 2.678, 2.667, 2.648	2-31, -1-31, -212, 012
8	2.593	16	2.600	-320
12	2.498	5	2.497	300
8	2.428	7, 1, 5	2.443, 2.437, 2.427	-2-22, 1-41, -1-32
22	2.220	13, 2, 5	2.211, 2.208, 2.204	310, 022, 2-32
12	2.173	8, 7, 6	2.176, 2.166, 2.163	1-42, -1-23, 0-23
28	2.039	13, 12, 2, 1, 2, 9, 2	2.057, 2.055, 2.045, 2.044, 2.041, 2.037, 2.032	-3-21, -340, -241, 131, 0-33, 221, -411
17	1.957	3, 4, 10, 8	1.967, 1.964, 1.953, 1.941	-213, 1-51, 140, 1-33
10	1.870	2, 3, 8, 3, 1	1.882, 1.877, 1.873, 1.871, 1.868	311, -431, 400, -402, 013
9	1.818	2, 3, 3, 2, 1	1.833, 1.831, 1.824, 1.821, 1.800	-313, 0-52, 3-12, -4-11, -2-41
8	1.771	5, 2, 2, 2	1.779, 1.779, 1.776, 1.770	-4-12, 050, 2-52, -3-23
18	1.704	7, 4, 2, 1, 12	1.712, 1.711, 1.709, 1.708, 1.704	-323, 2-13, -1-52, -441, -251
25	1.664	32, 24	1.665, 1.655	-1-14, -403
10	1.534	2, 12	1.534, 1.531	-304, 0-44
6	1.476	1, 4, 7, 2, 2	1.480, 1.479, 1.477, 1.476, 1.476	5-31, 213, 5-21, -5-11, 241
4	1.467	2, 3, 5	1.470, 1.468, 1.467	3-62, -433, 1-63
6	1.429	11	1.427	104
17	1.421	16, 5, 2, 8	1.422, 1.421, 1.420, 1.418	2-63, -224, -243, -404
5	1.391	3, 4	1.391, 1.391	-414, 1-71
5	1.341	4, 1, 2	1.341, 1.341, 1.339	061, 4-33, -4-42
6	1.294	2, 3, 4, 1	1.294, 1.293, 1.290, 1.290	204, 0-73, 4-53, 520
5	1.204	1, 3	1.210, 1.207	034, 6-51

\*For the calculated pattern, only reflections with intensities  $\geq 1$  are given. \*\*For the unit-cell parameters calculated from single-crystal data.

$\text{VO}_4$  tetrahedra,  $\text{MIO}_6$  octahedra [the  $\text{MI}$  sites are mainly occupied by  $\text{Fe}^{3+}$  in howardevansite, ( $\text{Fe}^{3+}, \text{Al}$ ) and ( $\text{Al}, \text{Fe}^{3+}$ ) in grigorievite or ( $\text{Fe}^{3+}, \text{Mg}, \text{Al}, \text{Ti}$ ) in koksharovite] and five-fold  $\text{MIIIO}_5$  polyhedra [ $\text{MII} = \text{Cu}^{2+}$  in howardevansite, ( $\text{Cu}, \text{Mg}$ ) in grigorievite and ( $\text{Mg}, \text{Fe}$ ) in koksharovite]. Two crystallographically independent  $\text{MIO}_6$  octahedra form edge-sharing dimeric clusters isolated from each other. The neighbouring octahedral dimers are connected *via* isolated  $\text{VO}_4$  tetrahedra. Each  $\text{Fe}(1)_2\text{O}_{10}$  dimer is connected with eight  $\text{VO}_4$  tetrahedra whereas each  $\text{Fe}(2)_2\text{O}_{10}$  dimer [or ( $\text{Al}, \text{Fe}$ ) $_2\text{O}_{10}$  dimer in grigorievite] is connected with ten  $\text{VO}_4$  tetrahedra. The linkage between the dimers is reinforced by the  $\text{MIIIO}_5$  polyhedra. Each  $\text{MIIIO}_5$  polyhedron shares one edge with the  $\text{Fe}(1)\text{O}_6$  octahedron and one edge with the  $\text{Fe}(2)\text{O}_6$  [or ( $\text{Al}, \text{Fe}$ ) $\text{O}_6$  in grigorievite] octahedron.

The sites occupied by large cations [(Na, Ca) in howardevansite and koksharovite, and the Cu(2) sites in

grigorievite] are located in tunnels running along [001]. In howardevansite (Hughes *et al.*, 1988), Na atoms occupy two independent sites forming the  $\text{Na}(1)\text{O}_6$  octahedra and the  $\text{Na}(2)\text{O}_7$  polyhedra (Fig. 5a). In koksharovite the site corresponding to Na(1) is fully occupied by Ca with Na and Mg admixtures [( $\text{Ca}_{0.70}\text{Na}_{0.16}\text{Mg}_{0.14}$ ): Ca site in Table 7 and Fig. 5c] whereas the site corresponding to Na(2) is mainly vacant, with only minor Na [( $\square_{0.86}\text{Na}_{0.14}$ ): ( $\square, \text{Na}$ ) site in Table 7 and Fig. 5c]. Moreover, this site in koksharovite is split around the inversion centre with a Ca-Ca distance of 0.681(8)  $\text{\AA}$  whereas in howardevansite and grigorievite cations occupying the corresponding sites are located at the inversion centre. Grigorievite is a Na-free and Ca-poor mineral (Table 3). In its structure, the site corresponding to Na(2) is vacant whereas the site corresponding to Na(1) is occupied by Cu [Cu(2) site in Table 8 and Fig. 5b]. We believe that the small amount of Ca in grigorievite is concentrated in this site (Table 8), which is

Table 5. X-ray powder diffraction data for grigorievite.

$I_{\text{obs}}$	$d_{\text{obs}}, \text{\AA}$	$I_{\text{calc}}^*$	$d_{\text{calc}}, \text{\AA}^{**}$	$hkl$
27	7.36	18	7.344	100
20	7.02	24	6.962	-110
17	6.10	11	6.069	001
29	4.718	19, 13	4.766, 4.658	-1-11, -111
24	4.417	10	4.411	020
13	3.928	9	3.908	1-21
26	3.671	14, 14	3.672, 3.668	200, -201
23	3.426	21	3.417	-121
100	3.141	92, 17	3.133, 3.129	-130, 021
92	3.044	7, 100	3.045, 3.035	2-11, 210
26	2.811	11, 23	2.819, 2.818	-112, -1-22
15	2.735	15	2.745	1-12
23	2.634	8, 12, 4	2.638, 2.635, 2.628	-212, 2-31, -1-31
12	2.555	1, 2, 16	2.574, 2.552, 2.551	-131, 0-32, -320
7	2.447	3, 3	2.448, 2.435	300, 220
13	2.376	5, 6, 2	2.383, 2.375, 2.369	-2-22, -1-32, 031
7	2.325	4, 4	2.321, 2.321	0-41, -330
5	2.268	2, 1	2.272, 2.267	-240, -302
7	2.226	3, 1	2.229, 2.218	112, 3-11
11	2.180	1, 11	2.194, 2.172	-331, 310
13	2.116	6, 6, 5	2.121, 2.110, 2.108	1-42, -1-23, 0-23
18	2.022	3, 9, 8, 5	2.031, 2.027, 2.016, 2.015	131, -340, -3-21, 221
11	1.941	3, 5, 2, 9, 4	1.947, 1.945, 1.945, 1.935, 1.933	3-41, -1-33, -213, 140, 1-51
4	1.888	5, 4	1.888, 1.880	1-33, 2-51
4	1.850	4	1.851	-431
5	1.800	4	1.791	0-52
6	1.731	6, 1, 2, 2, 5	1.742, 1.734, 1.728, 1.727, 1.726	-4-12, 2-52, -3-23, 3-51, 4-11
9	1.699	2, 7, 7	1.705, 1.698, 1.696	231, -251, -323
9	1.676	5, 6, 3, 1	1.677, 1.675, 1.674, 1.673	2-13, 302, -142, -1-52
22	1.636	19, 3, 28	1.639, 1.635, 1.632	-351, 321, -1-14
5	1.592	2, 3, 2	1.594, 1.593, 1.589	150, 1-53, -3-33
9	1.520	2, 9, 3	1.523, 1.520, 1.518	4-22, 3-61, 420
5	1.493	1, 1, 10	1.498, 1.493, 1.488	411, 3-23, 0-44
8	1.408	5, 1, 1, 10	1.409, 1.407, 1.406, 1.404	-224, 5-11, -503, 104
5	1.388	2, 12	1.390, 1.386	-4-33, 2-63
5	1.374	3, 4, 3, 1	1.379, 1.372, 1.371, 1.370	2-34, 1-71, -414, 303
4	1.337	4, 5	1.337, 1.336	-621, 061
3	1.265	2	1.264	0-73
3	1.258	4	1.258	4-53
3	1.238	3	1.238	-613
3	1.213	3	1.213	-1-73

\*For the calculated pattern, only reflections with intensities  $\geq 1$  are given. \*\*For the unit-cell parameters calculated from single-crystal data.

characterized by the longest mean cation–oxygen distance (Table 9). The Cu(2)-centred polyhedron is considered by us as flat square (Fig. 6); it could be also represented as a strongly Jahn-Teller distorted octahedron in which two Cu(2)–O(10) distances are 2.773(6) Å whereas the other four distances between the Cu(2) and O vary from 2.010 Å [Cu(2)–O(9)] to 2.104 Å [Cu(2)–O(3)] (Table 9).

The idealized structural formulae of the howardevansite-group members are given in Table 1. This group is structurally unique among minerals but some synthetic vanadates belonging to the same or closely related structure types are known; e.g.,  $\text{Mg}_3\text{Fe}^{3+}_4(\text{VO}_4)_6$  (Beskrovnyi *et al.*, 2006) is similar to the end-member koksharovite  $\text{CaMg}_2\text{Fe}^{3+}_4(\text{VO}_4)_6$ . They differ in the contents of the cation sites in channels. In  $\text{Mg}_3\text{Fe}^{3+}_4(\text{VO}_4)_6$  (Fig. 5d), the site corresponding to the Ca site in koksharovite is occupied

by Mg whereas the site corresponding to the Na site is vacant. All other known synthetic vanadates with howardevansite-like structures also contain only  $\text{Fe}^{3+}$  in the octahedral sites and have the same space group,  $P-1$ , and similar unit-cell parameters. These compounds with general formula  $\text{Me}_{3-4}\text{Fe}^{3+}_4(\text{VO}_4)_6$  are  $\beta\text{-Cu}_3\text{Fe}^{3+}_4(\text{VO}_4)_6$  (Lafontaine *et al.*, 1994),  $\text{Cu}_{2.5}\text{Fe}^{3+}_{4.333}(\text{VO}_4)_6$  (Belik *et al.*, 2001),  $\text{Li}_2\text{Cu}_2\text{Fe}^{3+}_4(\text{VO}_4)_6$  (Belik, 1999),  $\text{Zn}_3\text{Fe}^{3+}_4(\text{VO}_4)_6$  (Guskos *et al.*, 2005a),  $\text{Mn}_3\text{Fe}^{3+}_4(\text{VO}_4)_6$  and  $\text{Co}_3\text{Fe}^{3+}_4(\text{VO}_4)_6$  (Guskos *et al.*, 2005b).

Grigorievite differs from all other natural and synthetic vanadates with howardevansite-like structures by the ordering of octahedrally coordinated cations into the  $\text{Fe}^{3+}$ -dominant and Al-dominant sites (Fig. 5b). Grigorievite is close to synthetic  $\beta\text{-Cu}_3\text{Fe}^{3+}_4(\text{VO}_4)_6$  (Lafontaine *et al.*, 1994) in which Cu atoms occupy the

Table 6. Data collection information and structure refinement details for koksharovite and grigorievite.

Mineral	Koksharovite	Grigorievite
Temperature, K	293(2)	
Radiation and wavelength, Å	MoK $\alpha$ ; 0.71073	
Absorption coefficient $\mu$ , mm <sup>-1</sup>	5.418	6.854
F <sub>000</sub>	463	474
Crystal size, mm	0.03 × 0.05 × 0.09	0.04 × 0.08 × 0.12
Diffractometer	Xcalibur S CCD	
$\theta$ range for data collection, °	2.72–28.28	2.77–28.28
Index ranges	–10 ≤ <i>h</i> ≤ 10 –13 ≤ <i>k</i> ≤ 13 –8 ≤ <i>l</i> ≤ 8	–10 ≤ <i>h</i> ≤ 10 –12 ≤ <i>k</i> ≤ 12 –8 ≤ <i>l</i> ≤ 8
Reflections collected	7847	7600
Independent reflections	2355 ( <i>R</i> <sub>int</sub> = 0.1111)	2246 ( <i>R</i> <sub>int</sub> = 0.0570)
Independent reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	1643	1888
Structure solution	direct methods	
Refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>	
Number of refined parameters	177	169
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0788 w <i>R</i> 2 = 0.1008	<i>R</i> 1 = 0.0548 w <i>R</i> 2 = 0.1134
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1245 w <i>R</i> 2 = 0.1130	<i>R</i> 1 = 0.0701 w <i>R</i> 2 = 0.1198
GoF	1.094	1.149
Largest diff. peak and hole, e/Å <sup>3</sup>	1.023 and –1.196	1.609 and –0.708

same sites as in grigorievite, with the same coordination, and the only difference is the ordered substitution of Fe<sup>3+</sup> for Al in grigorievite. Note that triclinic  $\beta$ -Cu<sub>3</sub>Fe<sup>3+</sup><sub>4</sub>(VO<sub>4</sub>)<sub>6</sub> is chemically close to orthorhombic lyonsite Cu<sub>3+x</sub>(Fe<sup>3+</sup><sub>4-2x</sub>Cu<sub>2x</sub>)(VO<sub>4</sub>)<sub>6</sub> with 0 ≤ *x* ≤ 1 with a quite different structure (Hughes *et al.*, 1987; Pekov *et al.*, 2013b).

The assumption on the predominantly or even completely trivalent state of iron in howarddevansite-group minerals is based on four facts. (1) The cation–oxygen distances for Fe- and Al-dominant sites are too short for Fe<sup>2+</sup> (Table 9). (2) The general charge balance of the formulae requires Fe<sup>3+</sup>. (3) The bond valence sums indicate Fe<sup>3+</sup> (Tables 7 and 8). (4) All known synthetic vanadates with howarddevansite-like structures (including those studied by Mössbauer spectroscopy, Lafontaine *et al.*, 1994) contain only Fe<sup>3+</sup>. The trivalent state of Fe in these minerals is caused by the extremely oxidizing formation conditions, as attested both by mineralogical evidence (in these fumaroles, only minerals with species-defining S<sup>6+</sup>, As<sup>5+</sup>, Mo<sup>6+</sup>, Fe<sup>3+</sup>, and Tl<sup>3+</sup> are known for these elements, and V<sup>5+</sup> strongly predominates over V<sup>4+</sup>) and by geochemical evidence, like the fumarolic gas composition of the Second scoria cone, Tolbachik: Meniaylov *et al.*, 1980; Zelenski *et al.*, 2012).

Grigorievite contains 2.2–3.2 wt% MgO (Table 3). During the structure refinement, Mg was assigned to the Cu(1) site together with Cu<sup>2+</sup> (*e*<sub>ref</sub> = 23.6) but not at the octahedral sites. The existence of the synthetic compound Mg<sub>3</sub>Fe<sup>3+</sup><sub>4</sub>(VO<sub>4</sub>)<sub>6</sub> (Guskos *et al.*, 2005b; Beskrovnyi *et al.*, 2006), isostructural with  $\beta$ -Cu<sub>3</sub>Fe<sup>3+</sup><sub>4</sub>(VO<sub>4</sub>)<sub>6</sub> and structurally

Table 7. Coordinates, equivalent anisotropic displacement parameters (*U*<sub>eq</sub>, Å<sup>2</sup>) and bond valence totals ( $\sum$ s) for atoms and site population for koksharovite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	Site population**	$\sum$ s
V(1)	0.41434(18)	0.67055(16)	0.3907(2)	0.0077(3)	V <sub>0.97</sub> P <sub>0.03</sub>	5.08
V(2)	0.83771(18)	0.73729(16)	0.2743(2)	0.0077(3)	V <sub>0.97</sub> P <sub>0.03</sub>	5.10
V(3)	0.77817(18)	0.12779(16)	0.0972(2)	0.0078(3)	V <sub>0.97</sub> P <sub>0.03</sub>	5.15
Fe(1)	0.5469(2)	0.39402(19)	0.1225(3)	0.0091(4)	Fe <sub>0.47</sub> Mg <sub>0.29</sub> Al <sub>0.15</sub> Ti <sub>0.07</sub>	2.53
Fe(2)	0.2939(2)	0.98183(17)	0.4574(2)	0.0065(3)	Fe <sub>0.53</sub> Mg <sub>0.24</sub> Al <sub>0.15</sub> Ti <sub>0.08</sub>	2.82
Mg	0.7810(2)	0.7988(2)	0.7757(3)	0.0084(4)	Mg <sub>0.55</sub> Fe <sub>0.45</sub>	2.49
Ca	0.0140(11)	0.5320(6)	0.5436(9)	0.0136(14)	Ca <sub>0.35</sub> Na <sub>0.08</sub> Mg <sub>0.07</sub>	0.92
(□,Na)	0.023(7)	0.556(5)	0.995(9)	0.019(12)*	Na <sub>0.07</sub>	0.04
O(1)	0.4449(7)	0.8572(6)	0.4195(8)	0.0102(12)	O	2.07
O(2)	0.4679(7)	0.3436(6)	0.3708(8)	0.0108(13)	O	2.08
O(3)	0.7981(7)	0.5578(6)	0.2777(9)	0.0138(13)	O	1.99
O(4)	0.2235(7)	0.1634(7)	0.5118(9)	0.0153(14)	O	2.03
O(5)	0.2520(7)	0.0064(6)	0.1535(9)	0.0126(13)	O	2.01
O(6)	0.4697(7)	0.5804(6)	0.1667(8)	0.0101(13)	O	2.01
O(7)	0.7295(7)	0.7388(6)	0.0248(9)	0.0121(13)	O	2.03
O(8)	0.0537(7)	0.8177(7)	0.3220(9)	0.0185(15)	O	1.99
O(9)	0.2045(8)	0.5839(7)	0.3549(10)	0.0200(15)	O	2.07
O(10)	0.9991(7)	0.2404(7)	0.2157(10)	0.0203(15)	O	1.93
O(11)	0.7165(7)	0.0368(6)	0.2634(9)	0.0147(13)	O	1.98
O(12)	0.6652(8)	0.2440(7)	0.0800(10)	0.0217(15)	O	1.94

All site multiplicities *Q* = 2. \**U*<sub>iso</sub>; \*\*Refined taking into account the electron-microprobe data and fixed in the last stages of the refinement.



Table 8. Coordinates, equivalent isotropic thermal displacement parameters ( $U_{eq}$ , Å<sup>2</sup>) and bond valence totals ( $\sum s$ ) for atoms and site population for grigorievite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$	Site population*	$\sum s$
V(1)	0.40396(14)	0.66669(11)	0.38827(17)	0.0112(2)	V <sub>0.99</sub> P <sub>0.01</sub>	5.09
V(2)	0.84538(13)	0.73827(12)	0.28091(17)	0.0104(2)	V <sub>0.99</sub> P <sub>0.01</sub>	5.05
V(3)	0.76808(14)	0.12465(12)	0.09204(17)	0.0109(2)	V <sub>0.99</sub> P <sub>0.01</sub>	5.19
Fe	0.54933(15)	0.39565(13)	0.12342(19)	0.0119(3)	Fe <sub>0.47</sub> Al <sub>0.43</sub> Ti <sub>0.10</sub>	2.84
Al	0.30022(17)	0.98867(14)	0.4595(2)	0.0088(3)	Al <sub>0.67</sub> Fe <sub>0.33</sub>	3.04
Cu(1)	0.79085(14)	0.79860(12)	0.77639(16)	0.0182(3)	Cu <sub>0.68</sub> Mg <sub>0.32</sub>	2.34
Cu(2)	0	½	½	0.0309(5)	Cu <sub>0.63</sub> Ca <sub>0.20</sub>	1.61
O(1)	0.4422(5)	0.8589(5)	0.4213(7)	0.0121(9)	O	2.08
O(2)	0.4752(6)	0.3484(5)	0.3720(7)	0.0168(9)	O	2.15
O(3)	0.8076(6)	0.5554(5)	0.2923(8)	0.0205(10)	O	1.92
O(4)	0.2218(6)	0.1610(5)	0.5065(7)	0.0163(9)	O	2.06
O(5)	0.2675(6)	0.0102(5)	0.1641(7)	0.0172(9)	O	1.97
O(6)	0.4645(6)	0.5752(5)	0.1647(7)	0.0154(9)	O	2.10
O(7)	0.7352(6)	0.7389(5)	0.0250(7)	0.0173(9)	O	2.05
O(8)	0.0648(6)	0.8258(5)	0.3316(8)	0.0185(10)	O	2.03
O(9)	0.1895(6)	0.5813(6)	0.3599(9)	0.0254(11)	O	2.01
O(10)	-0.0085(7)	0.2379(6)	0.2063(8)	0.0305(13)	O	1.95
O(11)	0.7079(6)	0.0296(5)	0.2633(7)	0.0175(10)	O	2.00
O(12)	0.6499(7)	0.2404(5)	0.0710(8)	0.0227(11)	O	2.06

All site multiplicities  $Q = 2$ , except Cu(2) with  $Q = 1$ . \* Refined taking into account the electron-microprobe data and fixed in the last stages of the refinement.

Table 9. Selected interatomic distances (Å) in the structures of koksharovite and grigorievite.

Koksharovite		Grigorievite	
V(1) – O(9) 1.626(6)	V(2) – O(8) 1.646(6)	V(1) – O(9) 1.634(5)	V(2) – O(8) 1.645(4)
– O(1) 1.734(5)	– O(3) 1.711(5)	– O(2) 1.721(4)	– O(7) 1.721(5)
– O(2) 1.745(5)	– O(7) 1.725(5)	– O(1) 1.751(4)	– O(3) 1.734(5)
– O(6) 1.747(5)	– O(4) 1.760(6)	– O(6) 1.760(4)	– O(4) 1.777(4)
<V(1) – O> 1.713	<V(2) – O> 1.710	<V(1) – O> 1.716	<V(2) – O> 1.719
V(3) – O(12) 1.666(6)	Mg – O(10) 1.933(6)	V(3) – O(12) 1.670(5)	Al – O(11) 1.877(5)
– O(11) 1.671(6)	– O(5) 1.957(6)	– O(11) 1.676(4)	– O(4) 1.925(4)
– O(10) 1.720(6)	– O(2) 1.986(6)	– O(10) 1.707(5)	– O(1) 1.928(4)
– O(5) 1.765(5)	– O(7) 1.993(6)	– O(5) 1.776(5)	– O(8) 1.946(5)
<V(3) – O> 1.706	– O(4) 2.048(6)	<V(3) – O> 1.707	– O(5) 1.964(5)
	<Mg – O> 1.983		– O(1) 2.028(4)
Fe(1) – O(12) 1.969(6)		Fe – O(12) 1.893(5)	<Al – O> 1.945
– O(6) 1.998(5)	Fe(2) – O(11) 1.941(6)	– O(2) 1.956(4)	
– O(2) 2.030(5)	– O(1) 1.973(5)	– O(6) 1.957(4)	Cu(1) – O(10) 1.862(6)
– O(6) 2.068(5)	– O(4) 1.991(6)	– O(6) 2.020(4)	– O(7) 1.948(5)
– O(3) 2.075(6)	– O(8) 2.007(6)	– O(3) 2.079(5)	– O(4) 1.969(4)
– O(7) 2.135(6)	– O(5) 2.080(5)	– O(7) 2.153(5)	– O(5) 2.006(5)
<Fe(1) – O> 2.046	– O(1) 2.114(6)	<Fe – O> 2.010	– O(2) 2.069(5)
	<Fe(2) – O> 2.018		<Cu(1) – O> 1.971
Ca – O(9) 2.176(10)	Na – O(9) 2.44(5)	Cu(2) – O(9) 2.010(5)x 2	
– O(9) 2.236(10)	– O(9) 2.45(5)	– O(3) 2.104(5)x 2	
– O(3) 2.258(9)	– O(10) 2.76(4)	– O(10) 2.773(6)x 2	
– O(3) 2.348(9)	– O(3) 2.77(5)	<Cu(2) – O> 2.296	
– O(10) 2.438(8)	– O(8) 2.82(5)		
<Ca – O> 2.291	– O(3) 2.90(5)		
	– O(12) 2.98(5)		
	<Na – O> 2.73		

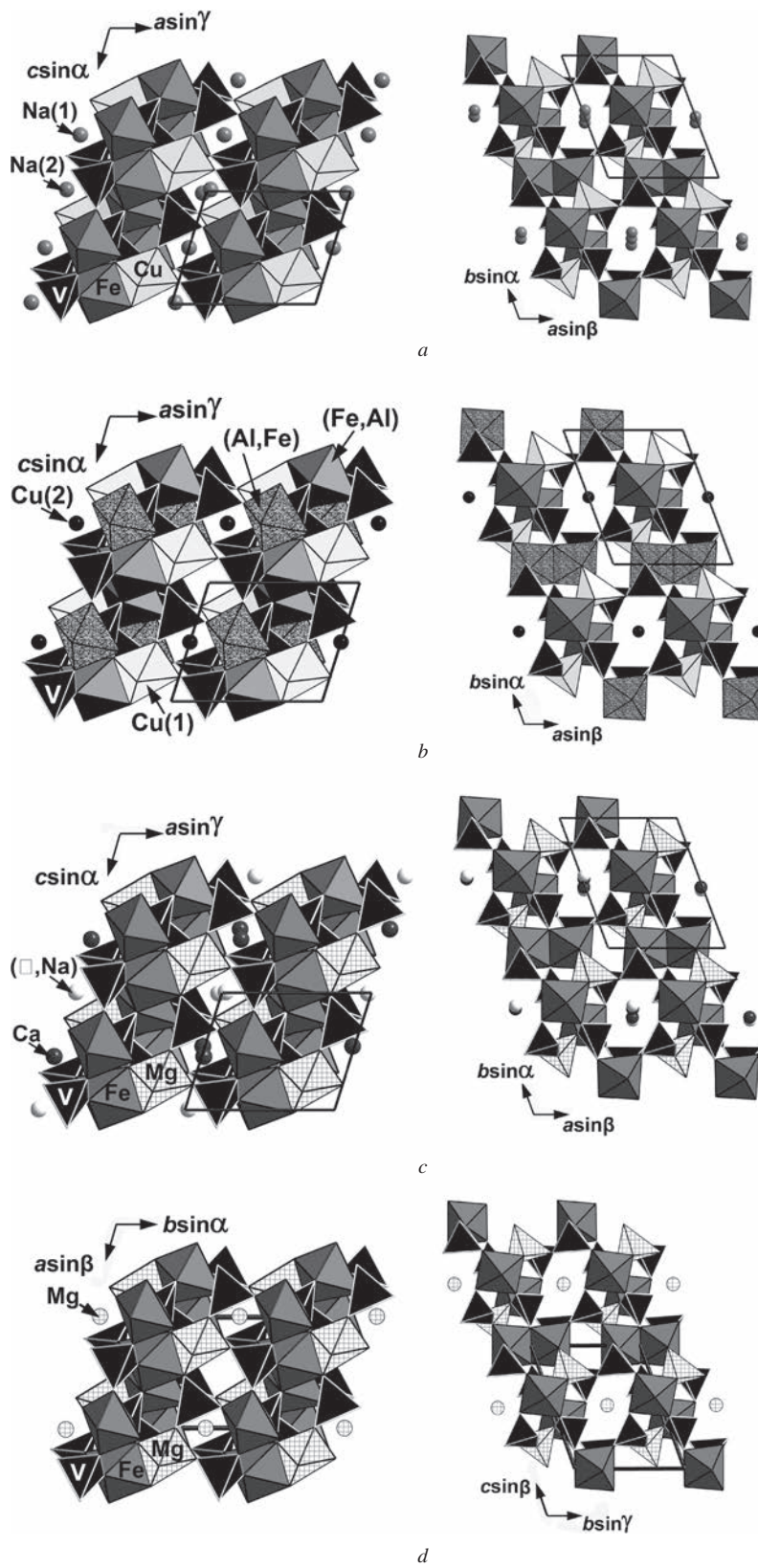


Fig. 5. Crystal structures of howardevansite (a: drawn after Hughes *et al.*, 1988), grigorievite (b), koksharovite (c) and synthetic  $\text{Mg}_3\text{Fe}^{3+}_4(\text{VO}_4)_6$  (d: drawn after Beskrovnyi *et al.*, 2006, with the unit-cell setting as reported in the cited paper). The unit cells are outlined.

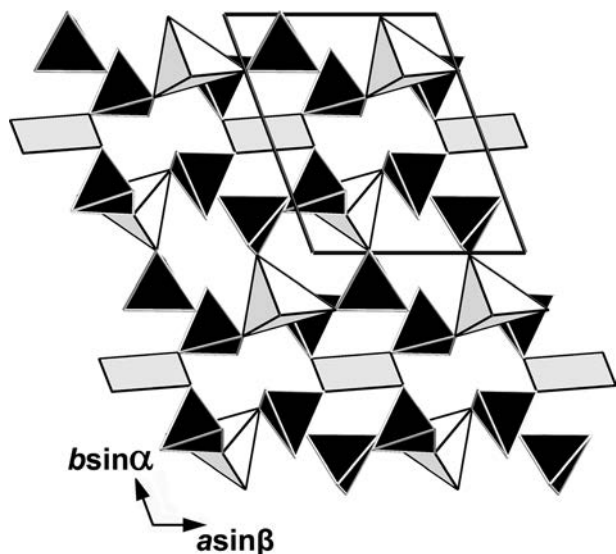


Fig. 6. The motif formed by V- and Cu-centred polyhedra in grigorievite. The  $\text{VO}_4$  tetrahedra are black,  $\text{Cu(1)O}_5$  and  $\text{Cu(2)O}_4$  groups are light-grey. The unit cell is outlined.

very close to grigorievite (Fig. 5b and d), confirms our assumption that Mg in this mineral substitutes for Cu. In  $\text{Mg}_3\text{Fe}^{3+}_4(\text{VO}_4)_6$ ,  $\text{Mg}^{2+}$  cations occupy the same sites as  $\text{Cu}^{2+}$  in  $\beta\text{-Cu}_3\text{Fe}^{3+}_4(\text{VO}_4)_6$  and in grigorievite. It should be noted that ziesite associated with grigorievite is represented by an Mg-bearing (2.4 wt% MgO) variety with the empirical formula  $(\text{Cu}_{1.58}\text{Mg}_{0.20}\text{Al}_{0.07}\text{Fe}_{0.05})_{\Sigma 1.90}\text{V}_{2.02}\text{O}_7$ . Synthetic analogues of ziesite with high contents of Mg substituting Cu were studied by Vogt & Müllerschbaum (1991).

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