



## Article

# New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. XVIII. Khrenovite, $\text{Na}_3\text{Fe}_2^{3+}(\text{AsO}_4)_3$ , the member with the highest sodium in the alluaudite supergroup

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### Abstract

The new alluaudite-group mineral khrenovite with the ideal, end-member formula  $\text{Na}_3\text{Fe}_2^{3+}(\text{AsO}_4)_3$  was found in the Arsenatnaya fumarole, Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. It is associated with aphtitalite-group sulfates, badalovite, calciojohillerite, nickenichite, johillerite, tilasite, svabite, achyrophanite, ozerovaitite, pansnerite, arsenatotitanite, anhydrite, sanidine, hematite, cassiterite, rutile and pseudobrookite. Khrenovite occurs as coarse prismatic crystals up to  $0.2 \times 0.3 \times 0.8$  mm and their clusters up to 1 mm across. It is transparent, honey-coloured, red-, orange- or yellow-brown, with vitreous lustre. Khrenovite is brittle, cleavage was not observed.  $D_{\text{calc}}$  is  $4.257 \text{ g cm}^{-3}$ . Khrenovite is optically biaxial (+),  $\alpha = 1.825(7)$ ,  $\beta = 1.834(7)$ ,  $\gamma = 1.845(7)$  and  $2V_{\text{meas}} = 80(10)^\circ$ . The chemical composition (wt.%, electron-microprobe) is:  $\text{Na}_2\text{O}$  11.47,  $\text{K}_2\text{O}$  1.23,  $\text{CaO}$  0.18,  $\text{MgO}$  0.01,  $\text{MnO}$  4.10,  $\text{CuO}$  4.27,  $\text{ZnO}$  1.99,  $\text{Al}_2\text{O}_3$  0.17,  $\text{Fe}_2\text{O}_3$  21.12,  $\text{SiO}_2$  0.08,  $\text{P}_2\text{O}_5$  0.01,  $\text{V}_2\text{O}_5$  0.10,  $\text{As}_2\text{O}_5$  56.03,  $\text{SO}_3$  0.02, total 100.78. The empirical formula calculated on the basis of 12 O apfu is  $(\text{Na}_{2.26}\text{K}_{0.16}\text{Ca}_{0.02}\text{Mn}_{0.35}\text{Cu}_{0.33}\text{Zn}_{0.15}\text{Al}_{0.02}\text{Fe}_{1.62})_{\Sigma 4.91}(\text{As}_{2.98}\text{Si}_{0.01}\text{V}_{0.01})_{\Sigma 3.00}\text{O}_{12}$ . Khrenovite is monoclinic,  $C2/c$ ,  $a = 12.2394(7)$ ,  $b = 12.7967(5)$ ,  $c = 6.6589(4)$  Å,  $\beta = 112.953(7)^\circ$ ,  $V = 960.37(10)$  Å<sup>3</sup> and  $Z = 4$ . The crystal structure was solved from single-crystal X-ray diffraction data with  $R_1 = 0.0287$ . Khrenovite is isostructural with other alluaudite-group minerals. Its structural formula simplified to the species-defining constituents is  ${}^{A(1)}\text{Na}{}^{A(2)}\text{Na}{}^{M(1)}\text{Na}{}^{M(2)}\text{Fe}_2^{3+}(\text{AsO}_4)_3$ . The mineral is named in honour of the Russian volcanologist and geologist Anatoly Petrovich Khrenov (1946–2016).

**Keywords:** khrenovite, new mineral, alluaudite group, arsenate, crystal structure, fumarole sublimate, Tolbachik volcano, Kamchatka

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### Introduction

This paper continues the series of descriptions of new arsenate mineral species found in the Arsenatnaya fumarole situated at the apical part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption 1975–1976 (NB GTFE), Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia ( $55^\circ 41' \text{N}$   $160^\circ 14' \text{E}$ , 1200 m a.s.l.). Twenty new minerals have been characterised in the previous papers of the series: yurmarinite  $\text{Na}_7(\text{Fe}^{3+}, \text{Mg}, \text{Cu})_4(\text{AsO}_4)_6$  (Pekov *et al.*, 2014a), two polymorphs of  $\text{Cu}_4\text{O}(\text{AsO}_4)_2$ , ericlxmanite and kozyrevskite (Pekov *et al.*, 2014b), popovite  $\text{Cu}_5\text{O}_2(\text{AsO}_4)_2$  (Pekov *et al.*, 2015a), structurally related shchurovskiyite  $\text{K}_2\text{CaCu}_6\text{O}_2(\text{AsO}_4)_4$  and dmisokolovite  $\text{K}_3\text{Cu}_5\text{AlO}_2(\text{AsO}_4)_4$

(Pekov *et al.*, 2015b), katiarsite  $\text{KTiO}(\text{AsO}_4)$  (Pekov *et al.*, 2016a), melanarsite  $\text{K}_3\text{Cu}_7\text{Fe}^{3+}\text{O}_4(\text{AsO}_4)_4$  (Pekov *et al.*, 2016b), pharmazincite  $\text{KZnAsO}_4$  (Pekov *et al.*, 2017), arsenowagnerite  $\text{Mg}_2(\text{AsO}_4)\text{F}$  (Pekov *et al.*, 2018c), arsenatotitanite  $\text{NaTiO}(\text{AsO}_4)$  (Pekov *et al.*, 2019a), the two isostructural minerals edtollite  $\text{K}_2\text{NaCu}_5\text{Fe}^{3+}\text{O}_2(\text{AsO}_4)_4$  and alumoedtollite  $\text{K}_2\text{NaCu}_5\text{AlO}_2(\text{AsO}_4)_4$  (Pekov *et al.*, 2019b), anatolyite  $\text{Na}_6(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}^{3+})_3\text{Al}(\text{AsO}_4)_6$  (Pekov *et al.*, 2019c), zubkovaite  $\text{Ca}_3\text{Cu}_3(\text{AsO}_4)_4$  (Pekov *et al.*, 2019d), pansnerite  $\text{K}_3\text{Na}_3\text{Fe}_6^{3+}(\text{AsO}_4)_8$  (Pekov *et al.*, 2020a), badalovite  $\text{NaNaMg}(\text{MgFe}^{3+})(\text{AsO}_4)_3$  (Pekov *et al.*, 2020b), calciojohillerite  $\text{NaCaMgMg}_2(\text{AsO}_4)_3$  (Pekov *et al.*, 2021a), yurgensonite  $\text{K}_2\text{SnTiO}_2(\text{AsO}_4)_2$  (Pekov *et al.*, 2021b) and paraberzeliite  $\text{NaCaCaMg}_2(\text{AsO}_4)_3$  (Pekov *et al.*, 2022).

Here we characterise khrenovite, a mineral with the end-member formula  $\text{Na}_3\text{Fe}_2^{3+}(\text{AsO}_4)_3$ . It belongs to the alluaudite group within the alluaudite supergroup and is the member of this supergroup richest in sodium (Hatert, 2019). In Pekov *et al.* (2018b) it was mentioned as “unnamed  $\text{Na}_3\text{Fe}_2^{3+}(\text{AsO}_4)_3$ ”.

Khrenovite (Cyrillic: хреновит) is named in honour of the Russian volcanologist and geologist Anatoly Petrovich Khrenov (1946–2016) who worked in the Institute of Volcanology and

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Seismology of the Far Eastern Branch of the Russian Academy of Sciences, Petropavlovsk-Kamchatsky, and, from 1993–2016, at the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM) of the Russian Academy of Sciences, Moscow. Dr. Khrenov has made significant contribution to studies of the Kamchatka volcanoes including Tolbachik.

Both the new mineral and its name (symbol Khr) have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2017–105, Pekov *et al.* 2018a). The holotype material is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow with the catalogue number 96190.

### Occurrence and general appearance

The active Arsenatnaya fumarole and its mineralogical features, including zonation in the distribution of mineral associations, were characterised by Pekov *et al.* (2014a, 2018b) and Shchipalkina *et al.* (2020).

Khrenovite is one of the rarest minerals in the Arsenatnaya fumarole. It was found in several specimens collected by us in July 2016 from the upper part of the zone enriched by alluaudite-group arsenates (zone Va; Shchipalkina *et al.*, 2020). It is situated at the depth of ~1.8 m from the surface. The temperature measured by us using a chromel–alumel thermocouple in this area was 430°C. We believe that khrenovite was formed at temperatures not lower than 430–450°C. It probably crystallised directly from the fumarolic gas phase as a volcanic sublimate.

The minerals associated with khrenovite are apthitalite-group sulfates (apthitalite, belomarinaite and metathénardite), badalovite, calciojohillerite, nickenichite, johillerite, tilasite, svabite, achyrophanite, ozerovaitite, pansnerite, arsenatrotitanite, anhydrite, sanidine (As-bearing variety), hematite, cassiterite, rutile and pseudobrookite.

Khrenovite occurs as coarse prismatic crystals (Fig. 1) up to 0.2 × 0.3 × 0.8 mm and their clusters up to 1 mm across. They contain numerous hematite inclusions and are located typically within aggregates of apthitalite-group sulfates overgrowing the surface of basalt scoria altered by fumarolic gas.



**Fig. 1.** Red-brown coarse prismatic crystals of khrenovite with colourless apthitalite and iron-black hematite. Field of view width: 1.5 mm; specimen #96190. Photo: I.V. Pekov & A.V. Kasatkin.

### Physical properties and optical data

Khrenovite is a transparent honey-coloured, red-, orange- or yellow-brown mineral. Its streak is yellowish and the lustre is vitreous. Khrenovite is brittle; cleavage or parting was not observed, and the fracture is uneven. The Mohs hardness is *ca.* 3½. The density calculated using the empirical formula and unit-cell volume obtained from single-crystal X-ray diffraction data is 4.257 g cm<sup>-3</sup>.

In plane-polarised transmitted light, khrenovite is weakly pleochroic, with the following absorption scheme: X (pale yellow-brownish) > Y ≈ Z (nearly colourless). It is optically biaxial (+), α = 1.825(7), β = 1.834(7), γ = 1.845(7) (589 nm), 2V<sub>meas.</sub> = 80(10)° and 2V<sub>calc.</sub> = 85°. Dispersion of optical axes is strong, *r* > *v*. The optical orientation is presumably Y = *b* (by analogy with other alluaudite-group arsenates).

### Raman spectroscopy

The Raman spectrum of khrenovite (Fig. 2) was obtained on a randomly orientated crystal using an EnSpectr R532 instrument (Dept. of Mineralogy, Moscow State University) with a green laser (532 nm) at room temperature. The output power of the laser beam was ~16 mW. The spectrum was processed using the EnSpectr expert mode program in the range from 4000 to 100 cm<sup>-1</sup> with the use of a holographic diffraction grating with 1800 lines per cm<sup>-1</sup> and a resolution of 6 cm<sup>-1</sup>. The diameter of the focal spot on the sample was ~16 μm. The back-scattered Raman signal was collected with a 40× objective; signal acquisition time for a single scan of the spectral range was 1000 ms and the signal was averaged over 50 scans.

The Raman spectrum of khrenovite was interpreted according to Nakamoto (1986). The bands with maxima at 961, 859 and 809 cm<sup>-1</sup> correspond to As<sup>5+</sup>–O stretching vibrations of AsO<sub>4</sub><sup>3-</sup> anions and the band with maximum at 475 cm<sup>-1</sup> and shoulder at 537 cm<sup>-1</sup> is assigned to Fe<sup>3+</sup>–O stretching vibrations. Bands with frequencies lower than 450 cm<sup>-1</sup> correspond to bending vibrations of AsO<sub>4</sub> tetrahedra, Mn–O and Cu–O stretching vibrations and lattice modes. The absence of bands with frequencies higher than 900 cm<sup>-1</sup> indicates the absence of groups with O–H, C–H, C–O, N–H, N–O and B–O bonds.

### Chemical composition

Chemical studies of khrenovite were performed using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 20 nA and a 10 μm beam diameter.

The chemical data are given in Table 1. Contents of other elements with atomic numbers >6 were below detection limits. The empirical formula calculated on the basis of 12 O atoms per formula unit (apfu) is (Na<sub>2.26</sub>K<sub>0.16</sub>Ca<sub>0.02</sub>Mn<sub>0.35</sub>Cu<sub>0.33</sub>Zn<sub>0.15</sub>Al<sub>0.02</sub>Fe<sub>1.62</sub>)<sub>Σ4.91</sub>(As<sub>2.98</sub>Si<sub>0.01</sub>V<sub>0.01</sub>)<sub>Σ3.00</sub>O<sub>12</sub>. The idealised, end-member formula, in accordance with the actual nomenclature of the alluaudite group (Hatert, 2019), is Na<sub>3</sub>Fe<sub>2</sub><sup>3+</sup>(AsO<sub>4</sub>)<sub>3</sub>.

### X-ray crystallography and crystal structure determination

The powder X-ray diffraction (XRD) data for khrenovite (Supplementary Table S1) were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with cylindrical

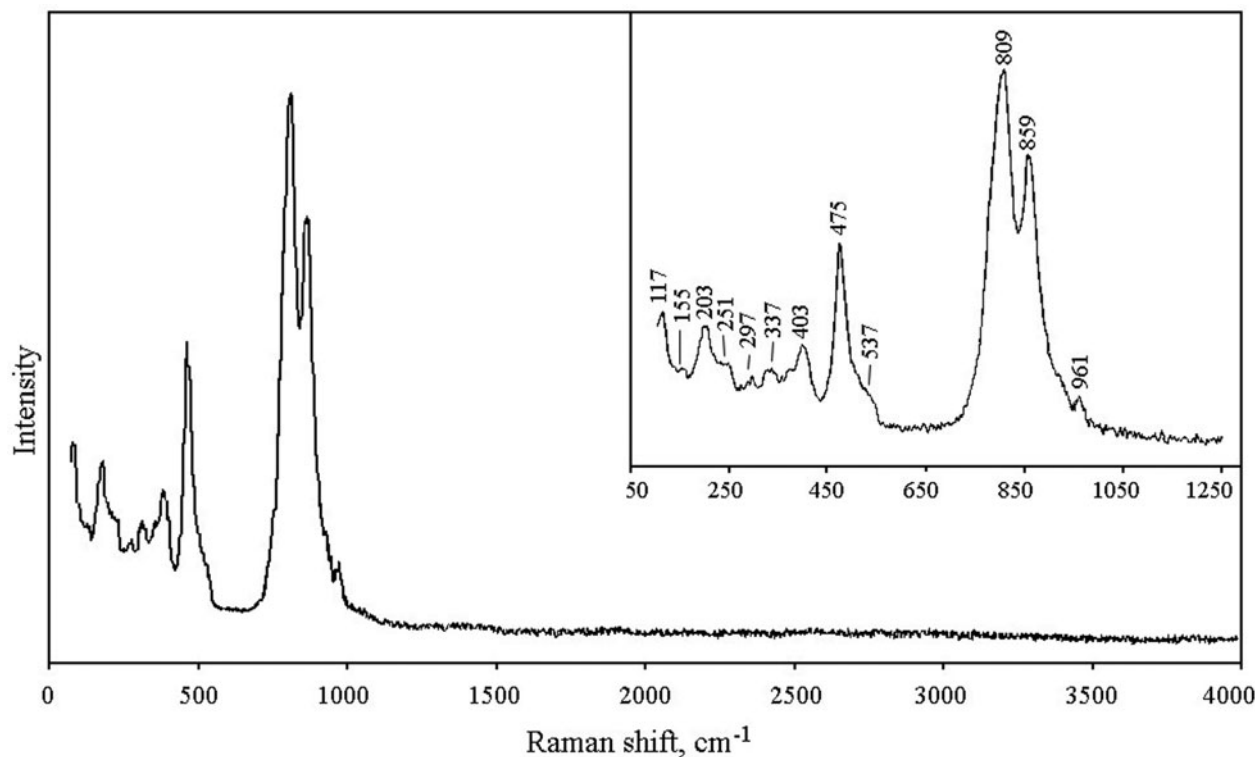


Fig. 2. The Raman spectrum of khrenovite.

image plate detector ( $r = 127.4$  mm) using Debye-Scherrer geometry,  $\text{CoK}\alpha$  radiation (rotating anode with VariMAX microfocussing optics), 40 kV, 15 mA and 12 min exposure. The angular resolution of the detector is  $0.045^\circ 2\theta$  (pixel size 0.1 mm). The data were integrated using the software package *osc2Tab* (Britvin *et al.*, 2017). The unit-cell parameters refined from the powder data are:  $a = 12.248(6)$ ,  $b = 12.818(4)$ ,  $c = 6.657(4)$  Å,  $\beta = 112.97(4)^\circ$  and  $V = 962(1)$  Å<sup>3</sup>. These values slightly differ from ones obtained from the single crystal data, probably due to some chemical variations from crystal to crystal.

Single-crystal XRD studies of khrenovite were carried out using an Xcalibur S diffractometer equipped with a CCD detector. A full sphere of three-dimensional data was collected. Intensity

data were corrected for Lorentz and polarisation effects. The crystal structure of the new mineral was refined using the calciojohillerite structure (Pekov *et al.*, 2021a) as the starting model with the *SHELX* software package (Sheldrick, 2015) to  $R = 0.0287$  on the

Table 2. Crystal data, data collection information and structure refinement details for khrenovite.

Formula	(Na <sub>0.93</sub> Mn <sub>0.07</sub> ) $\Sigma_{1.00}$ (Na <sub>0.71</sub> K <sub>0.06</sub> ) $\Sigma_{0.77}$ (Na <sub>0.54</sub> Mn <sub>0.34</sub> Zn <sub>0.12</sub> ) $\Sigma_{1.00}$ (Fe <sub>1.70</sub> Cu <sub>0.30</sub> ) $\Sigma_{2.00}$ (AsO <sub>4</sub> ) <sub>3</sub>
Formula weight	612.39
Crystal system, space group, Z	Monoclinic, C2/c, 4
$a$ , $b$ , $c$ (Å)	12.2394(7), 12.7967(5), 6.6589(4)
$\beta$ (°)	112.953(7)
$V$ (Å <sup>3</sup> )	960.37(10)
$F(000)$	1146
$\mu$ (mm <sup>-1</sup> )	14.275
Absorption correction	multi-scan
Crystal dimensions (mm)	0.20 × 0.31 × 0.53
Diffractometer	Xcalibur S CCD
Temperature (K)	293
Radiation	Mo K $\alpha$ , $\lambda = 0.71073$ Å
$\theta$ range (°)	3.184–34.776
Range of $h$ , $k$ , $l$	–19 → 19, –20 → 20, –10 → 10
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	11997, 2014, 1906
$R_{\text{int}}$	0.049
Refinement on	$F^2$
Extinction coefficient	0.00109(13)
$R1$ and $wR2$ for $I > 2\sigma(I)$	0.0287, 0.0630
$R1$ and $wR2$ for all data	0.0314, 0.0644
No. of parameters refined	99
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	2.08, –1.60
Goof	1.124
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2 + 3.5750P]$ $P = ([\text{max}(0 \text{ or } F_o^2)] + 2Fc^2)/3$

Table 1. Chemical composition (wt.%) of khrenovite.

Constituent	Average*	Range	S.D.	Probe standard
Na <sub>2</sub> O	11.47	11.20–11.93	0.24	jadeite
K <sub>2</sub> O	1.23	1.11–1.36	0.09	KTiOPO <sub>4</sub>
CaO	0.18	0.05–0.28	0.07	CaSiO <sub>3</sub>
MgO	0.01	0.00–0.06	0.01	olivine
MnO	4.10	3.47–4.99	0.47	MnTiO <sub>3</sub>
CuO	4.27	3.54–4.82	0.44	Cu
ZnO	1.99	1.69–2.29	0.23	ZnS
Al <sub>2</sub> O <sub>3</sub>	0.17	0.07–0.25	0.07	jadeite
Fe <sub>2</sub> O <sub>3</sub>	21.12	20.49–22.28	0.59	FeS <sub>2</sub>
SiO <sub>2</sub>	0.08	0.00–0.13	0.05	jadeite
P <sub>2</sub> O <sub>5</sub>	0.01	0.00–0.06	0.01	KTiOPO <sub>4</sub>
V <sub>2</sub> O <sub>5</sub>	0.10	0.04–0.26	0.08	V
As <sub>2</sub> O <sub>5</sub>	56.03	55.32–57.21	0.74	GaAs
SO <sub>3</sub>	0.02	0.00–0.06	0.02	ZnS
Total	100.78			

\*Averaged for seven spot analyses; S.D. – standard deviation

**Table 3.** Coordinates, equivalent displacement parameters ( $U_{\text{eq}}$ , Å<sup>2</sup>) and bond-valence sums (BVS) for atoms in the structure of khrenovite.\*

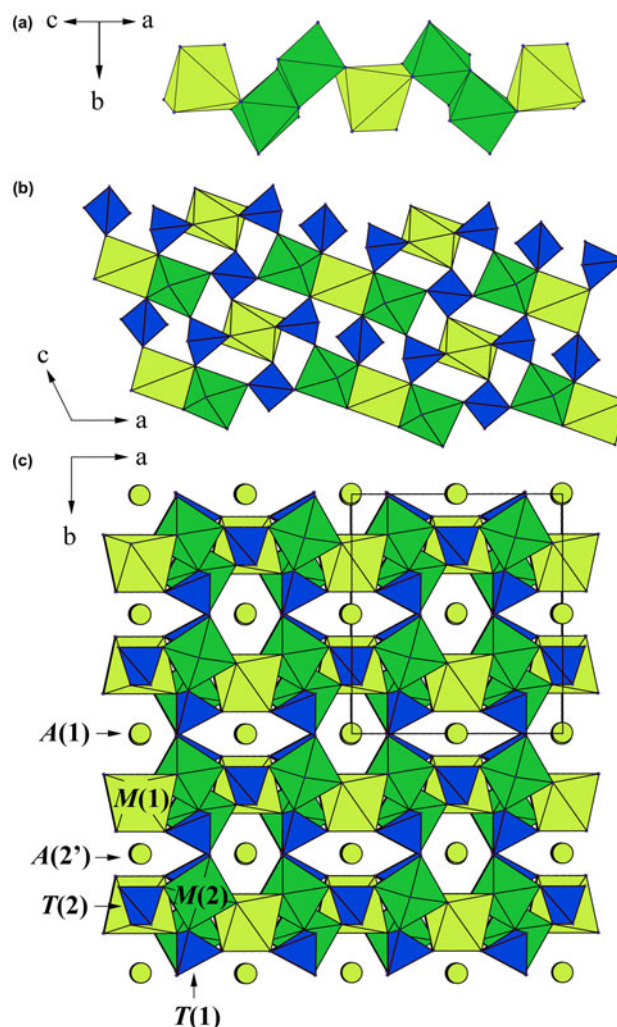
Site	Wyckoff	x	y	z	$U_{\text{eq}}$	BVS
A(1)	4b	1/2	0	0	0.0211(6)	1.13
A(2)'	4e	0	-0.0032(2)	1/4	0.0363(10)	0.61
M(1)	4e	0	0.26718(7)	1/4	0.0198(3)	1.59
M(2)	8f	0.27982(3)	0.65651(3)	0.36646(6)	0.00928(11)	2.74
T(1)	4e	0	-0.28049(3)	1/4	0.00918(9)	4.93
T(2)	8f	0.24240(2)	-0.10768(2)	0.12979(4)	0.01081(8)	5.03
O(1)	8f	0.45267(18)	0.70456(16)	0.5245(3)	0.0148(4)	1.97
O(2)	8f	0.10588(18)	0.63648(16)	0.2421(3)	0.0165(4)	1.96
O(3)	8f	0.32826(19)	0.66826(16)	0.1121(3)	0.0155(4)	2.01
O(4)	8f	0.1143(2)	0.40674(19)	0.3088(4)	0.0229(5)	2.04
O(5)	8f	0.22535(18)	0.81821(15)	0.3297(3)	0.0138(3)	1.89
O(6)	8f	0.3274(2)	0.50781(16)	0.3873(4)	0.0210(4)	1.98

\*Bond-valence parameters were taken from Gagne and Hawthorne (2015). Bond-valence sums were calculated taking into account cation distribution.

basis of 1906 independent reflections with  $I > 2\sigma(I)$ . Crystal data, data collection information and structure refinement details for khrenovite are given in Table 2, coordinates, equivalent displacement parameters of atoms and bond-valence sums in Table 3, and selected interatomic distances in Table 4. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

## Discussion

Khrenovite possesses the alluaudite-type structure (Fig. 3) based upon a three-dimensional framework composed of zig-zag chains of edge-sharing  $M(1)O_6$  and  $M(2)O_6$  octahedra connected with  $T(1)O_4$  and  $T(2)O_4$  tetrahedra. The  $M$ -octahedral chains consist of  $[M(2)_2O_{10}]$  dimers of distorted  $M(2)O_6$  octahedra connected *via* distorted  $M(1)O_6$  octahedra isolated from one another (Fig. 3a).  $T(1)O_4$  tetrahedra share all vertices with the  $M$ -centred octahedra to form the (010) heteropolyhedral layers (Fig. 3b) whereas each  $T(2)O_4$  tetrahedron shares three vertices with the  $MO_6$  octahedra of one layer and the fourth vertex with the octahedron of the adjacent layer, thus linking the layers to a three-dimensional framework. Two large-cation positions A(1) and A(2)' are situated in channels running through the framework parallel to [001] (Fig. 3c). The  $M$  and A cation sites are labelled according to the

**Fig. 3.** The crystal structure of khrenovite: (a) chain of  $[M(2)_2O_{10}]$  dimers connected *via* isolated  $M(1)O_6$  octahedra; (b) heteropolyhedral layer; (c) general view of the crystal structure projected along the  $c$  axis, with the unit cell outlined.

scheme proposed by Hatert *et al.* (2000) and revisited by Krivovichev *et al.* (2013).

The first channel can be described as a chain of  $A(1)O_6$  cubes sharing common faces, and the second as a chain of  $A(2)O_8$

**Table 4.** Selected interatomic distances (Å) in the structure of khrenovite.

$A(1)O_6$ polyhedron	$M(1)O_6$ octahedron	$T(1)O_4$ tetrahedron
A(1)–O(4)×2	M(1)–O(4)×2	T(1)–(O1)×2
A(1)–O(2)×2	M(1)–O(1)×2	T(1)–O(2)×2
A(1)–O(4)×2	M(1)–O(3)×2	<T(1)–O>
<A(1)–O>	<M(1)–O>	
$A(2)'O_8$ polyhedron	$M(2)O_6$ octahedron	$T(2)O_4$ tetrahedron
A(2)'–O(6)×2	M(2)–O(2)	T(2)–O(4)
A(2)'–O(6)×2	M(2)–O(6)	T(2)–O(6)
A(2)'–O(1)×2	M(2)–O(3)	T(2)–O(3)
A(2)'–O(3)×2	M(2)–O(1)	T(2)–O(5)
<A(2)'–O>	M(2)–O(5)	<T(2)–O>
	<M(2)–O>	

polyhedra connected *via* common edges. Average  $A(1)$ -O and  $A(2)'$ -O distances are 2.411 and 2.744 Å, respectively. Both  $A(1)$  and  $A(2)'$  sites are Na-dominant and, based on sizes of polyhedra, we assume admixtures of Mn in the  $A(1)$  site and K in the partially vacant  $A(2)'$  site. The  $A(1)$  site occupancy was refined using scattering curves of Na vs Mn, and  $A(2)'$  using the scattering curve of Na (observed scattering of 9.24 electrons per site). There were no maxima in the difference-Fourier map in the  $A(1)'$  site, indicating the absence of  $\text{Cu}^{2+}$  in the channels.

In khrenovite the larger  $M(1)\text{O}_6$  octahedron has an average  $M$ -O distance of 2.263 Å, and the smaller  $M(2)\text{O}_6$  octahedron has an  $M$ -O distance of 2.042 Å. Based on the polyhedra sizes and data on hatertite (Krivovichev *et al.*, 2013), we assign Na, Mn and Zn to the  $M(1)$  site, and  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  to the  $M(2)$  site. The occupancy of the  $M(1)$  site was refined using scattering curves of Na, Mn and Zn with the sum of their occupancy factors fixed at 1.00, for the  $M(2)$  site the Fe-scattering curve was used (the  $e_{\text{ref}}$  for this site is 26.08). Admixed Cu cations were added to  $M(2)$  similarly to cation distribution in hatertite and for consistency with chemical data.

Both  $T(1)\text{O}_4$  and  $T(2)\text{O}_4$  tetrahedra are  $\text{As}^{5+}$ -centred, insignificant admixtures of V and Si were not considered during refinement.

The crystal chemical formula of the structurally studied khrenovite crystal can be written, taking into account electron microprobe data and ignoring minor admixtures of Al, Ca, Mg, Si, V, P and S, as:  $A(1)(\text{Na}_{0.93}\text{Mn}_{0.07})A(2)'(\text{Na}_{0.71}\text{K}_{0.06}\square_{0.23})M(1)(\text{Na}_{0.54}\text{Mn}_{0.34}\text{Zn}_{0.12})M(2)(\text{Fe}_{1.70}\text{Cu}_{0.30})(\text{AsO}_4)_3$ , which is close to the averaged composition obtained by electron microprobe (Table 1). Thus, the structural formula of the mineral, simplified to the species-defining constituents, is  $A(1)\text{Na}A(2)'\text{Na}M(1)\text{Na}M(2)\text{Fe}_2^+(\text{AsO}_4)_3$  that gives the end-member formula  $\text{Na}_3\text{Fe}_2^+(\text{AsO}_4)_3$ .

Khrenovite is the first mineral of the alluaudite supergroup with Na prevailing in the  $M(1)$  position and the third, after alluaudite and yazganite, with trivalent cations prevailing in the  $M(2)$  site; in all other known natural alluaudite-type arsenates and phosphates, divalent cations dominate in  $M(1)$  and di- or trivalent cations in  $M(2)$  (Hatert, 2019). In addition, a synthetic alluaudite-type arsenate  $\text{Na}_3\text{In}_2^+(\text{As}_3\text{O}_4)_3$  is known (Lii and Ye, 1997; Khorari *et al.*, 1997). It is the compound most similar to khrenovite in terms of crystal chemistry. A synthetic compound  $\text{Na}_3\text{Fe}_2^+(\text{AsO}_4)_3$  with the alluaudite-type structure is unknown, though two other modifications of this arsenate have been synthesised, namely trigonal phase ( $R\bar{3}c$ ,  $a = 13.698$  and  $c = 18.59$  Å, d'Yvoire *et al.*, 1988) with the structure very similar to that of yurmarinite  $\text{Na}_7(\text{Fe}^{3+}, \text{Mg}, \text{Cu})_4(\text{AsO}_4)_6$  discovered in the same Arsenatnaya fumarole (Pekov *et al.*, 2014a), and a cubic phase with the garnet structure ( $Ia\bar{3}d$ ,  $a = 12.25$  Å, Ouerfelli *et al.*, 2008). It is not excluded that significant admixtures of divalent cations in the  $M$  and/or  $A$  sites stabilise the alluaudite-like structure of khrenovite.

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**Competing interests.** The authors declare none.

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