



Article

Medvedevite, $\text{KMn}^{2+}\text{V}_2^{5+}\text{O}_6\text{Cl}\cdot 2\text{H}_2\text{O}$, a new fumarolic mineral from the Tolbachik fissure eruption 2012–2013, Kamchatka Peninsula, Russia

Andrey P. Shablinskii¹ , Margarita S. Avdontceva², Lidiya P. Vergasova³, Stanislav K. Filatov^{2*} , Evgenia Yu. Avdontseva², Alexey V. Povolotskiy⁴ , Svetlana V. Moskaleva³, Anatoly A. Kargopoltsev³, Sergey N. Britvin² and Olga U. Shoretts¹

¹Institute of Silicate Chemistry of the Russian Academy of Sciences, Makarova Emb. 2., 199034, Saint Petersburg, Russia; ²Institute of Earth Sciences, Saint Petersburg State University, University Emb. 7/9., 199034, Saint Petersburg, Russia; ³Institute of Volcanology and Seismology, Far Eastern Branch of the Russian Academy of Sciences, Piip Boulevard 9, 683006, Petropavlovsk-Kamchatsky, Russia; and ⁴Institute of Chemistry, Saint Petersburg State University, University Emb. 7/9., 199034, Saint Petersburg, Russia

Abstract

Medvedevite, $\text{KMn}^{2+}\text{V}_2^{5+}\text{O}_6\text{Cl}\cdot 2\text{H}_2\text{O}$, is a new mineral discovered in the Toludskoe lava field, formed during the 2012–2013 Tolbachik fissure eruption. The mineral occurs as thin acicular transparent bright red crystals up to 0.15 mm. Medvedevite is associated with thénardite, halite, apthitalite, leonite, kieserite, eugsterite and syngenite. The empirical formula calculated on the basis of 13+ positive charge units for the anhydrous part and $2\text{H}_2\text{O}$ is $(\text{K}_{1.02}\text{Na}_{0.03})_{\Sigma 1.05}\text{Mn}_{0.95}^{2+}(\text{V}_{1.92}\text{S}_{0.05}^{6+}\text{Si}_{0.04})_{\Sigma 2.01}\text{O}_{6.02}\text{Cl}_{0.96}\cdot 2\text{H}_2\text{O}$. The crystal structure of medvedevite was determined using single-crystal X-ray diffraction data: monoclinic crystal system, the space group is $P2_1/c$, $a = 7.1863(2)$, $b = 10.1147(3)$, $c = 12.7252(4)$ Å, $\beta = 106.243(3)^\circ$, $V = 888.04(5)$ Å³, $Z = 4$ and $R_1 = 0.029$. The concept of ‘structural unit’ and ‘interstitial complex’ could be applied to the crystal structure of medvedevite. The structural units in medvedevite are based on the high bond-valence V^{5+}O_5 polyhedra which share edges and link into $[\text{V}_2\text{O}_6]$ chains elongated along the a axis. The interstitial complexes consist of Mn^{2+} , K^+ cations and H_2O groups and occupy the interstices between structural units. The mineral is optically biaxial (+), with $\alpha = 1.782(2)$, $\beta = 1.786(2)$, $\gamma = 1.792(2)$, $2V(\text{calc}) = 41^\circ$ ($\lambda = 589$ nm). The seven strongest lines of the powder XRD pattern are [d , Å (I , %) (hkl)]: 7.79(100)(011); 5.70(11)(110); 4.75(14)(11 $\bar{2}$); 3.89(29)(022); 3.25(53)(031); 2.958(79)(213); and 2.850(33)(220). The mineral has been named in honour of the Russian geologist and chemist Robert Alexandrovich Medvedev (1939–2005).

Keywords: medvedevite, new mineral, vanadate, crystal structure, fumarolic minerals, Tolbachik volcano, Kamchatka peninsula

(Received 1 March 2022; accepted 4 April 2022; Accepted Manuscript published online: 13 May 2022; Associate Editor: G. Diego Gatta)

Introduction

The last eruption of the Tolbachik volcano (Kamchatka Peninsula, Russian Far East) occurred almost ten years ago. It was termed the 2012–2013 Tolbachik fissure eruption. The extensive post-eruption activity led to the formation of fumarolic fields with structurally and chemically diverse mineralisation. The diversity and originality of this mineralisation is due to a combination of unique conditions and mechanisms: these are high temperatures, atmospheric pressure, oxidising conditions and gas transport of most components. Sulfate and arsenate mineralisations are the most widespread in terms of the number of mineral species. At the moment, more than 350 mineral species have been reliably established and more than 120 new mineral species have been discovered on the Tolbachik volcano (Pekov *et al.*, 2020a). Five chloro-vanadates have been described on the Tolbachik volcano, including leningradite $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}$ (Vergasova *et al.*,

1990; Siidra *et al.*, 2007), averievite $\text{Cu}_6\text{O}_2(\text{VO}_4)_2\text{Cl}_2\cdot n(\text{K,Cs,Rb})\text{Cl}$ (Starova *et al.*, 1997; Vergasova *et al.*, 1998), yaroshevskite $\text{Cu}_9\text{O}_2(\text{VO}_4)_4\text{Cl}_2$ (Pekov *et al.*, 2013), dokuchaevite $\text{Cu}_8\text{O}_2(\text{VO}_4)_3\text{Cl}_3$ (Siidra *et al.*, 2019b) and aleutite $\text{Cu}_5\text{O}_2(\text{AsO}_4)(\text{VO}_4)(\text{Cu}_{0.5}\square_{0.5})\text{Cl}$ (Siidra *et al.*, 2019a). Vanadate mineralisation is represented, for example, by the following minerals: pseudolyonsite $\text{Cu}_3(\text{VO}_4)_2$ (Zelenski *et al.*, 2011), udinaite $\text{NaMg}_4(\text{VO}_4)_3$ (Pekov *et al.*, 2018b), kainotropite $\text{Cu}_4\text{Fe}^{3+}\text{O}_2(\text{V}_2\text{O}_7)(\text{VO}_4)$ (Pekov *et al.*, 2020b). Vergasova and Filatov (2012, 2016), Pekov *et al.* (2018a, 2020a) and Vergasova *et al.* (2022) investigated the fumarolic activity and mineralisation of Tolbachik eruptions.

Herein we describe medvedevite (Russian Cyrillic: медведевит), a new mineral, ideally $\text{KMn}^{2+}\text{V}_2\text{O}_6\text{Cl}\cdot 2\text{H}_2\text{O}$, found in 2020 on the Toludskoe lava field, formed during the 2012–2013 Tolbachik fissure eruption, Kamchatka Peninsula, Russia. Medvedevite (symbol Mvv) has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2021-082a, Shablinskii *et al.*, 2022). The mineral has been named in honour of the Russian geologist and chemist Robert Alexandrovich Medvedev (1939–2005). He was a member of several geological parties of the Steppe Expedition (Makinsk, Tselinograd Region,

*Author for correspondence: Stanislav K. Filatov, Email: filatov.stanislav@gmail.com

Cite this article: Shablinskii A.P., Avdontceva M.S., Vergasova L.P., Filatov S.K., Avdontseva E.Y.u., Povolotskiy A.V., Moskaleva S.V., Kargopoltsev A.A., Britvin S.N. and Shoretts O.U. (2022) Medvedevite, $\text{KMn}^{2+}\text{V}_2^{5+}\text{O}_6\text{Cl}\cdot 2\text{H}_2\text{O}$, a new fumarolic mineral from the Tolbachik fissure eruption 2012–2013, Kamchatka Peninsula, Russia. *Mineralogical Magazine* 86, 478–485. <https://doi.org/10.1180/mgm.2022.38>

Kazakh SSR), and worked on uranium deposits in Northern and Central Kazakhstan. The geological prospecting works resulted in the discovery of the three major ore regions of Kazakhstan with 62 uranium deposits.

Under the leadership of Robert Alexandrovich Medvedev and with his direct participation progressive methods were introduced for the determination of gases in various alloys of rare earth metals. As a qualified specialist with a pronounced research approach, Robert Alexandrovich worked constantly on the improvement of laboratory methods in order to increase their quality and reduce the time for performing analyses. Many of his initiatives formed the basis of rationalisation proposals and scientific and technical work. Thus, Robert Alexandrovich Medvedev created a department for active leaching, desorption and electrolysis in the chemical and metallurgical workshop in order to extract gold from 'poor' raw materials and obtain finished products at the Ural Electrolytic Copper Refinery 'Uralelectromed'.

The type specimen of medvedevite is deposited in the Mineralogical Museum of Saint-Petersburg State University (St. Petersburg, Russia) under catalogue number 1/19900.

Occurrence and association

The holotype material was collected (11.09.2020) on the Toludskoe lava field, which was formed during the 2012–2013 Tolbachik fissure eruption. The mineral was found in the stalactites of a lava cave (Fig. 1). The size of the stalactite was 3 m × 2 m. The stalactite had a basalt core, and the thickness of the mineral deposits was 3 mm. Thin needle transparent bright red crystals of medvedevite were found included in thénardite crystals. Medvedevite occurs in association with thénardite, halite, aphthitalite, leonite, kieserite, eugsterite and syngenite.

General appearance and physical properties

Medvedevite occurs as red well-formed prismatic or fine acicular crystals up to 0.15 mm long (Figs 2, 3). The streak is red and the lustre is vitreous. Cleavage is perfect {010}. The calculated density based on the empirical formula and powder unit-cell parameters obtained from the powder X-ray diffraction (XRD) data is 2.69 g/cm³.



Fig. 1. Lava cave of the Toludskoe lava field (2020). Photo by A.A. Kargopol'tsev.

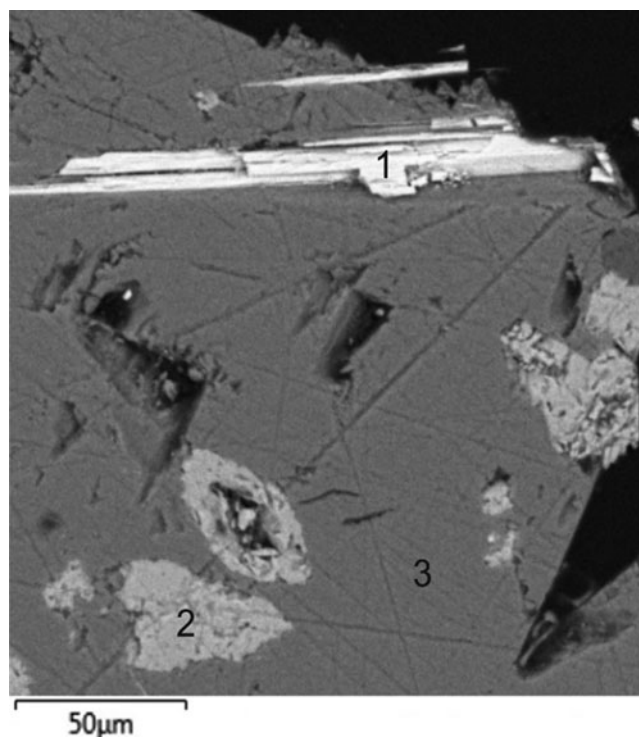


Fig. 2. Crystals of medvedevite (1) with aphthitalite (2) and thénardite (3). Scanning electron microscopy image, specimen #6.

The mineral is optically biaxial (+), with $\alpha = 1.782(2)$, $\beta = 1.786(2)$, $\gamma = 1.792(2)$ and $2V(\text{calc}) = 41^\circ$ ($\lambda = 589$ nm). Orientation: $Y = b$. Pleochroism is weak, with the following absorption scheme: Z (dark red) > X (bright red). The Gladstone–Dale compatibility index (Mandarino, 1981) based on the ideal formula and unit-cell parameters obtained from single crystal XRD data is calculated as $1 - (K_p/K_c) = 0.004$ (superior).

Chemical composition

The chemical composition of medvedevite was studied using a TESCAN "Vega3" electron microprobe equipped with an Oxford Instruments X-max 50 silicon drift energy-dispersive spectroscopy system, operated at 20 kV and 760 pA, with a beam size of 220 nm. Analytical results are given in Table 1. The data processing was done using Aztec software and an X-MAX-80 mm² detector. The empirical formula calculated on the basis of 13+ positive charge units for the anhydrous part and 2H₂O is $(K_{1.02}Na_{0.03})_{\Sigma 1.05}Mn_{0.95}(V_{1.92}S_{0.05}Si_{0.04})_{\Sigma 2.01}O_{6.02}Cl_{0.96} \cdot 2H_2O$. The simplified formula is $(K,Na)Mn(V,S,Si)_2O_6Cl \cdot 2H_2O$. The ideal formula is $KMn^{2+}V_2^{5+}O_6Cl \cdot 2H_2O$, which requires K₂O 12.96, MnO 19.52, V₂O₅ 50.05, H₂O 9.91, Cl 9.76, -O = Cl -2.20, total 100 wt.%.

Powder X-ray diffraction

The powder XRD data were collected using a Rigaku R-AXIS RAPID II diffractometer (Gandolfi mode with CoK α) and handled using the domestic software (Britvin *et al.*, 2017). Medvedevite is monoclinic, $P2_1/c$, $a = 7.1831(5)$, $b = 10.1121(9)$, $c = 12.737(1)$ Å, $\beta = 106.16(3)^\circ$, $V = 888.6(4)$ Å³ and $Z = 4$. The measured and calculated powder diffraction patterns are given in Table 2.

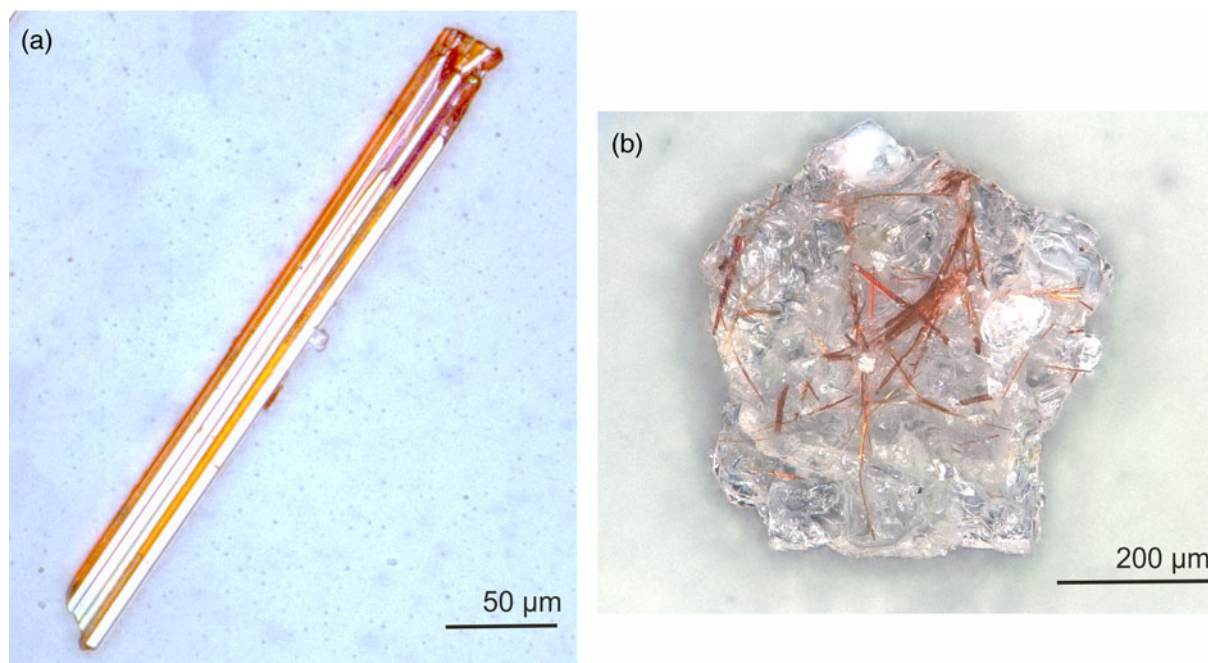


Fig. 3. (a) Red acicular crystal of medvedevite; (b) crystals of medvedevite in thénardite [specimen #6].

Single-crystal X-ray diffraction

A single crystal of medvedevite was studied using a Rigaku XtaLab Synergy-S diffractometer equipped with a high-speed direct-action detector HyPix-6000HE. The study was carried out by means of microfocus monochromatic MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) with frame widths 1.0° in ω and 180 s counting time for each frame. The data were interpolated into the *CrysAlisPro* software (2015) for further processing. An absorption correction was introduced using the *SCALE3 ABSPACK* algorithm. The crystal structure was solved by direct methods and refined by least-square techniques in the monoclinic space group $P2_1/c$ to $R_1 = 0.029$ ($wR_2 = 0.077$) for 2152 unique observed reflections with $I \geq 2\sigma(I)$ using the *SHELX* program package (Sheldrick, 2015) within the *Olex2* shell (Dolomanov *et al.*, 2009). The hydrogen atoms of O8 were placed in calculated positions and refined using a ‘riding’ model and were included with $U_{\text{iso}}(\text{H})$ set to $1.5 U_{\text{eq}}(\text{O})$ and an O–H bond length restrained to 0.92 \AA . The hydrogen atoms of O7 were located from the inspection of difference-Fourier maps using the *DFIX* command. Crystallographic data and refinement parameters, atomic

Table 1. Chemical data (in wt %) for medvedevite.

Constituent	Mean	Range	S.D.	Probe standard
Na ₂ O	0.26	0.00–1.05	0.49	NaCl
SiO ₂	0.60	0.32–2.72	0.79	sanidine
SO ₃	1.22	0.75–3.42	0.81	ZnS
K ₂ O	13.48	12.94–14.57	0.57	sanidine
V ₂ O ₅	49.15	46.64–51.26	1.30	V
MnO	19.06	18.20–19.91	0.54	MnTiO ₃
Cl	9.52	9.08–10.01	0.34	NaCl
H ₂ O*	10.16			
O=Cl ₂	-2.15			
Total	101.30			

* Calculated for 2H₂O in the empirical formula
S.D. – standard deviation

coordinates and isotropic displacement parameters, atomic anisotropic displacement parameters and selected bond lengths are summarised in Tables 3–5. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

Crystal structure

The crystal structure of medvedevite belongs to a new structure type. The concept of ‘structural unit’ and ‘interstitial complex’ (Hawthorne, 1983; Schindler *et al.*, 2000a, 2000b) could be applied to crystal structure of medvedevite. The structural units in medvedevite are based on the high bond-valence V⁵⁺O₅ polyhedra which share edges and link into [V₂O₆] chains elongated along the *a* axis (Figs 4, 5). The interstitial complexes consist of Mn²⁺, K⁺ cations and H₂O groups and occupy the interstices between structural units.

Each of the two independent VO₅ polyhedra includes two short vanadyl (1.642–1.658 Å) and three long equatorial (1.894–2.022 Å) bonds producing 2+3 coordination. The O atoms that participate the vanadyl bonds are in *cis* configuration and connected only with one V atom. The O atoms that participate in the equatorial bonds are connected with three V atoms and involved in the forming of chains *via* edges. The Mn1 site is coordinated octahedrally by four O atoms of vanadium polyhedra ($\langle \text{Mn1-O} \rangle$ 2.149–2.177 Å), one chlorine ($\langle \text{Mn1-Cl1} \rangle$ 2.471 Å) and one O atom of the H₂O molecule ($\langle \text{Mn-O7} \rangle$ 2.175 Å). The K1 site is surrounded by five oxygen atoms ($\langle \text{K1-O} \rangle$ 2.747–3.181 Å) and two chlorine atoms ($\langle \text{K1-Cl1} \rangle$ 3.089–3.194 Å).

Raman spectroscopy

The Raman spectrum was measured with a Horiba Jobin-Yvon LabRam HR800 spectrometer with a spectral resolution of

Table 2. Powder X-ray diffraction data (d in Å) for medvedevite.

l_{obs}	d_{obs}	$l_{\text{calc.}}$	$d_{\text{calc.}}$	h	k	l
100	7.79	100	7.794	0	1	1
2	6.11	2	6.127	0	0	2
11	5.70	16	5.699	1	1	0
4	5.38	3	5.380	1	0	2
5	5.23	6	5.234	0	1	2
7	5.06	7	5.056	0	2	0
14	4.75	18	4.750	1	1	2
29	3.89	36	3.897	0	2	2
8	3.77	4	3.782	0	1	3
		7	3.761	1	1	2
53	3.25	53	3.250	0	3	1
		9	3.174	0	2	3
19	3.05	16	3.058	0	0	4
		8	2.997	1	1	4
79	2.958	48	2.966	2	1	1
		50	2.957	2	1	3
33	2.850	24	2.850	2	2	0
		20	2.846	2	2	2
5	2.670	6	2.672	1	2	3
9	2.614	13	2.617	0	2	4
3	2.590	4	2.591	1	3	2
5	2.465	8	2.469	1	1	4
5	2.299	4	2.301	1	3	3
		4	2.297	1	3	4
3	2.087	3	2.101	3	1	4
		4	2.077	1	1	6
		7	2.039	0	0	6
9	2.023	3	2.026	2	0	4
		3	2.019	2	0	6
		4	1.995	0	5	1
18	1.979	19	1.980	0	3	5
		4	1.960	2	4	1
2	1.941	3	1.942	3	1	2
18	1.843	14	1.845	2	4	2
		15	1.842	2	4	4
12	1.797	21	1.796	4	0	2
		3	1.751	4	1	1
7	1.747	4	1.749	2	1	5
		5	1.744	2	1	7
2	1.633	5	1.632	4	2	0
		4	1.587	0	4	6
8	1.573	5	1.572	4	3	1
		6	1.571	4	3	3
3	1.558	5	1.559	0	5	5
2	1.526	3	1.526	2	6	1
8	1.501	8	1.503	2	2	6
		8	1.499	2	2	8

The seven strongest lines are shown in bold.

For the calculated pattern, only reflections with intensities ≥ 1 are given.

*The values of $d_{\text{calc.}}$ are calculated on the basis of unit cell parameters refined by powder XRD data.

3 cm^{-1} . The CW He–Ne laser with a wavelength of 632.8 nm and a power of 10 mW was used to excite the scattering. The laser beam was focused on the sample surface with 50 \times objective lens. The scattering light was collected with the same objective, and the spectrum was recorded twice within 60 seconds.

The Raman spectrum of medvedevite is shown in Fig. 6. The observed Raman bands and their assignments (according to Baran *et al.*, 1987; Yao *et al.*, 2018) for medvedevite $\text{KMn}^{2+}\text{V}_2^{5+}\text{O}_6\text{Cl}\cdot 2\text{H}_2\text{O}$ are given in the Table 6. The bands around 475 cm^{-1} and 837 cm^{-1} were assigned to symmetric and antisymmetric stretching vibrations V–O–V, respectively. Baran *et al.* (1987) note that similar stretching vibrations are observed at similar frequencies for V_2O_5 . Raman bands below 400 cm^{-1} are related to VO_2 rocking, twisting and chain deformation vibrations (Yao *et al.*, 2018). Thus, the Raman spectroscopy data agree with the

Table 3. Crystallographic data and refinement parameters for medvedevite.

Crystal data	
Chemical formula	$\text{KMn}^{2+}\text{V}_2^{5+}\text{O}_6\text{Cl}\cdot 2\text{H}_2\text{O}$
M_r	363.4
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	7.1863 (2), 10.1147 (3), 12.7252 (4)
β ($^\circ$)	106.243 (3)
V (Å 3)	888.04 (5)
Z	4
Radiation type	MoK α
μ (mm^{-1})	4.24
Data collection	
Crystal size (mm)	0.12 \times 0.07 \times 0.05
Data collection	
Diffractometer	XtaLAB Synergy, Single source at home/near, HyPix
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2333, 2333, 2152
R_{int}	0.014
$(\sin \theta/\lambda)_{\text{max}}$ (Å $^{-1}$)	0.682
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.079, 1.08
No. of reflections	2333
No. of parameters	128
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ ($e^- \text{Å}^{-3}$)	1.83, -0.50

XRD data, and the main contribution to the vibrational spectra is made by vanadium polyhedra linked into chains through a bridging oxygen.

FTIR spectroscopy

The FTIR spectrum was measured in transmission mode (crystal on a KBr plate) on a Bruker Hyperion 2000 IR microscope connected to a Bruker Vertex 70 FTIR spectrometer. The spectrum with a resolution of 4 cm^{-1} was recorded by an InGaAs detector cooled with liquid nitrogen.

The FTIR spectrum of medvedevite is shown in Fig. 7. The IR spectrum clearly identifies the water that is part of the studied mineral by the O–H stretching vibrations, which correspond to the bands in the region of 3250, 3410 and 3570 cm^{-1} . Moreover, the bending vibrations of molecular water show bands in the region of 1660 and 1600 cm^{-1} . The position of the bands of these vibrations is similar to the vibrations in metarossite (Frost *et al.*, 2004) (Table 6).

Discussion

Medvedevite $\text{KMn}^{2+}\text{V}_2^{5+}\text{O}_6\text{Cl}\cdot 2\text{H}_2\text{O}$ is structurally related to delrioite $\text{Sr}(\text{VO}_3)(\text{H}_2\text{O})_4$ (Thompson and Sherwood, 1959), metarossite $\text{Ca}(\text{VO}_3)_2(\text{H}_2\text{O})_2$ (Kelsey and Barnes, 1960), rossite $\text{Ca}(\text{VO}_3)(\text{H}_2\text{O})_4$ (Ahmed and Barnes, 1963), metadelrioite $\text{CaSr}(\text{V}_2\text{O}_6)(\text{OH})_2$ (Smith, 1970), munirite $\text{NaVO}_3(\text{H}_2\text{O})_2$ (Butt and Mahmood, 1983), metamunirite NaVO_3 (Kato and Takayama, 1984), dickthomssenite $\text{MgV}_2\text{O}_6(\text{H}_2\text{O})_7$ (Hughes *et al.*, 2001), ansermetite $\text{MnV}_2\text{O}_6(\text{H}_2\text{O})_4$ (Brugger *et al.*, 2003) and calciodelrioite $\text{Ca}(\text{VO}_3)(\text{H}_2\text{O})_4$ (Kampf *et al.*, 2012). The crystal structure of these minerals contain the same structural unit – divanadate V_2O_6 chains with edge-shared VO_5 polyhedra. According to (Schindler *et al.*, 2000a, 2000b) Lewis basicities of

Table 4. Atomic coordinates and displacement parameters (Å²) for medvedevite.

Atom	x/a	y/b	z/c	U_{iso}^* / U_{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.74567(6)	0.27571(5)	0.74400(3)	0.0133(1)	0.0117(2)	0.0142(2)	0.0138(2)	-0.0012(2)	0.0034(1)	-0.0041(1)
V1	0.42507(6)	0.02015(4)	0.60171(3)	0.0069(1)	0.0054(2)	0.0093(2)	0.0061(2)	-0.0011(1)	0.0015(1)	-0.0005(1)
V2	-0.07462(6)	0.01480(4)	0.60328(3)	0.0070(1)	0.0053(2)	0.0092(2)	0.0065(2)	0.0010(1)	0.0017(1)	-0.0001(1)
K1	0.20334(12)	0.34309(8)	0.62908(8)	0.0363(2)	0.0280(4)	0.0268(4)	0.0492(5)	0.0044(3)	0.0023(3)	-0.0003(3)
Cl1	0.84519(14)	0.14346(9)	0.91386(6)	0.0322(2)	0.0451(5)	0.0297(4)	0.0197(4)	-0.0004(4)	0.0058(3)	0.0068(3)
O1	0.6533(3)	-0.0189(2)	0.5605(1)	0.0155(4)	0.0072(8)	0.032(1)	0.0069(8)	0.0012(8)	0.0015(7)	-0.0032(7)
O2	0.1495(3)	0.0417(2)	0.5554(1)	0.0134(4)	0.0064(8)	0.0234(1)	0.0110(8)	-0.0010(7)	0.0035(7)	-0.0031(7)
O3	0.0013(3)	-0.0972(2)	0.7001(2)	0.0180(4)	0.016(1)	0.0202(1)	0.0175(9)	0.0051(8)	0.0038(8)	0.0085(8)
O4	0.4945(3)	0.1579(2)	0.6697(2)	0.0192(4)	0.0145(9)	0.018(1)	0.023(1)	-0.0030(8)	0.0023(8)	-0.0102(8)
O5	0.4393(3)	-0.1031(2)	0.6892(2)	0.0210(4)	0.017(1)	0.0227(1)	0.024(1)	0.0005(8)	0.0068(8)	0.0121(9)
O6	-0.0855(3)	0.1600(2)	0.6617(2)	0.0182(4)	0.019(1)	0.0153(1)	0.024(1)	-0.0010(8)	0.0107(8)	-0.0060(8)
O7	0.6429(4)	0.4051(3)	0.6032(2)	0.0330(6)	0.049(2)	0.0276(1)	0.021(1)	0.001(1)	0.007(1)	0.004(1)
O8	0.7007(5)	0.6717(3)	0.6114(3)	0.063(1)	0.042(2)	0.0305(2)	0.105(3)	-0.001(1)	0.003(2)	0.003(2)
H7A	0.681(9)	0.382(7)	0.544(3)	0.09(2)*						
H7B	0.667(6)	0.492(1)	0.611(3)	0.03(1)*						
H8A	0.8113	0.6844	0.6675	0.094*						
H8B	0.6287	0.7451	0.6159	0.094*						

Table 5. Selected bond lengths (Å) for medvedevite.

Mn1-O4	2.149 (2)	V1-O4	1.642 (2)
Mn1-O5 ⁱⁱ	2.150 (2)	V1-O5	1.655 (2)
Mn1-O6 ⁱ	2.156 (2)	V1-O1	1.898 (2)
Mn1-O7	2.175 (3)	V1-O2	1.914 (2)
Mn1-O3 ⁱⁱ	2.177 (2)	V1-O1 ⁱⁱⁱ	1.982 (2)
Mn1-Cl1	2.4714 (9)	<V1-O> ₅	1.82
<Mn1-φ> ₆	2.38	V2-O3	1.651 (2)
K1-O4	2.747 (2)	V2-O6	1.658 (2)
K1-O6	2.897 (2)	V2-O2	1.894 (2)
K1-O5 ⁱⁱ	2.986 (2)	V2-O1 ^v	1.908 (2)
K1-O3 ^{vii}	3.006 (2)	V2-O2 ^{iv}	2.022 (2)
K1-O2	3.181 (2)	<V2-O> ₅	1.83
K1-Cl1 ⁱⁱ	3.089 (1)	H7A-O7	0.893 (10)
K1-Cl1 ^{vi}	3.194 (1)	H7B-O7	0.894 (10)
<K1-φ> ₇	3.01	<H7-O> ₂	0.89
K1-O8 ^{viii}	3.323 (5)	H8A-O8	0.917
K1-O7	3.326 (3)	H8B-O8	0.916
<K1-φ> ₉	3.08	<H8-O> ₂	0.92

this structural unit can vary from 0.14 to 0.22 valence units (vu). The calculation of Lewis basicity for the structural unit and Lewis acidity for the interstitial complex in the medvedevite crystal structure lets us to determine the role of the H₂O groups, stability of the minerals and possible response to dehydration of the medvedevite crystal structure.

The bond-valence calculations were performed using empirical parameters taken from Brown and Altermatt (1985) (Table 7). The bond-valence calculations and values of the bond lengths can confirm the valence of Mn (e.g. Levi and Aurbach, 2014). According to Levi and Aurbach (2014), the average bond length for MnO₆ is 2.18–2.23 Å for Mn²⁺, 2.02–2.08 Å for Mn³⁺, 1.89–1.92 Å for Mn⁴⁺. The average bond length of the MnO₅Cl polyhedra in the crystal structure of medvedevite is 2.21 Å. Therefore, the valence of Mn in the medvedevite is 2+ according to analysis of bond-valence and bond lengths data. If we calculate the bond valence sums (BVS) for MnO₅Cl polyhedra in the crystal structure of medvedevite using *r*₀ parameter for Mn²⁺ (Brown and Altermatt, 1985), the BVS is 2.23 vu. And if we calculate BVS for MnO₅Cl polyhedra in the crystal structure of medvedevite using *r*₀ parameters for Mn³⁺ (Brown and Altermatt, 1985), the BVS is decreased (2.09 vu). Therefore, the valence of Mn is 2+.

The knowledge of the coordination numbers of cation and anions in the structural unit lets us calculate the Lewis basicity of the structural unit (Hawthorne, 1985; Schindler et al., 2000a, Hawthorne and Schindler, 2008; Hawthorne, 2015). In the structural unit of medvedevite, the average coordination number of O is 3.2. Therefore, there are 19 bonds in the crystal structure that involve O atoms of the structural unit. Within the structural unit, there are 10 bonds in the VO₅ polyhedra. The number of additional bonds required from outside the structural unit is 9. Thus, the Lewis basicity of a structural unit is 2/9 = 0.22 vu.

The interstitial complex in the medvedevite crystal structure is [¹⁷K⁶Mn²⁺(H₂O)_d(H₂O)_e¹⁴Cl]. The Lewis acidity of the interstitial complex can be defined as its charge divided by the number of bonds to the structural unit: $(a + 2b + 3c - f) / [(am + bn + cl) + d - f(q - 1)]$, where *a* = number of monovalent cations, *b* = number of divalent cations, *c* = number of trivalent cations, *d* = transformer H₂O groups, *e* = non-transformer H₂O groups, *f* = monovalent anions, *m*, *n*, *l* and *q* = coordination numbers.

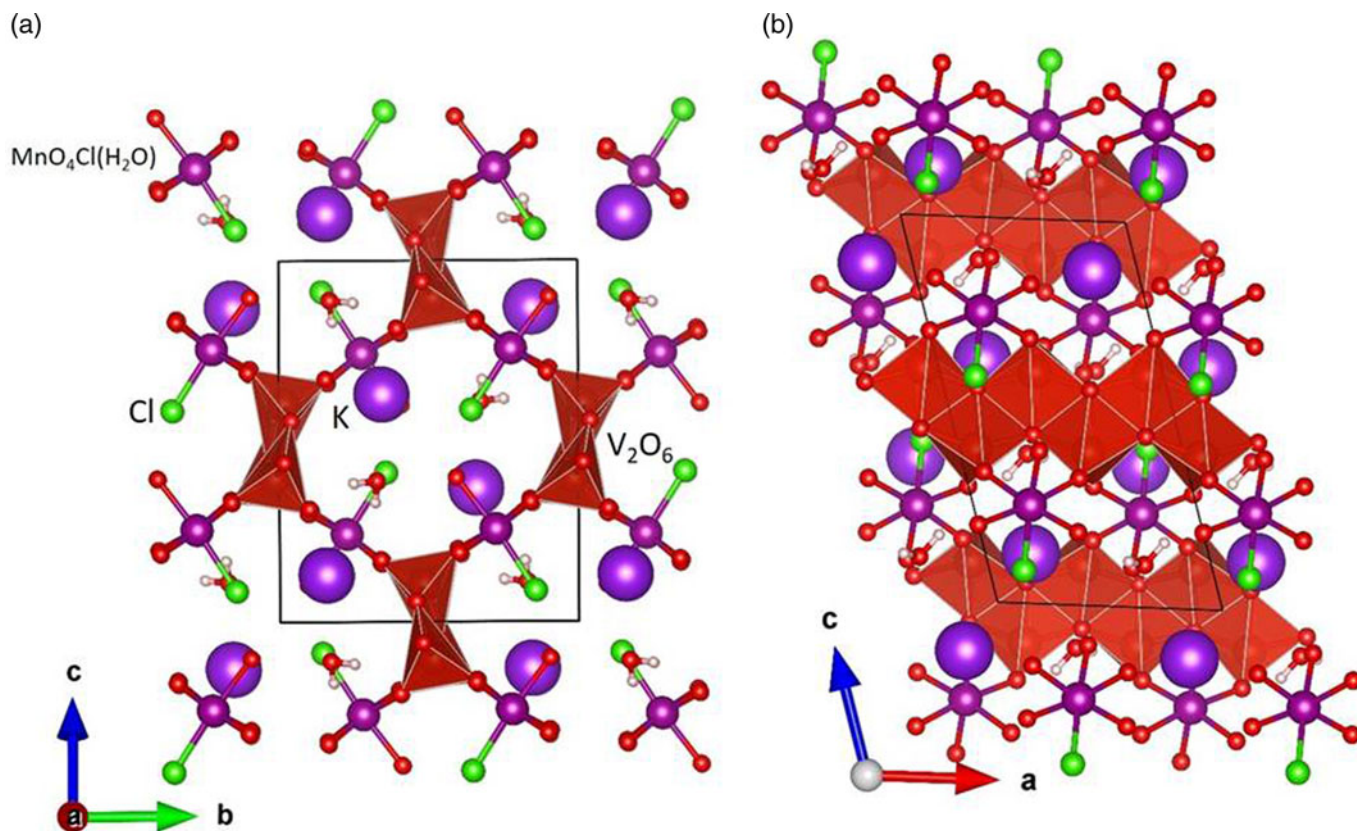


Fig. 4. Crystal structure of medvedevite: (a) the *cb* section; (b) the *ac* section. The unit cell is outlined.

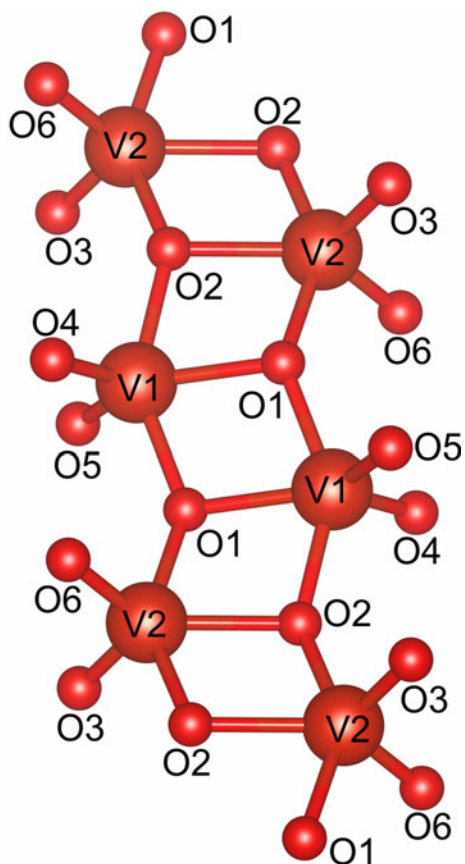


Fig. 5. Divanadate V_2O_6 chain in the crystal structure of medvedevite with edge-shared VO_5 polyhedra (structural unit).

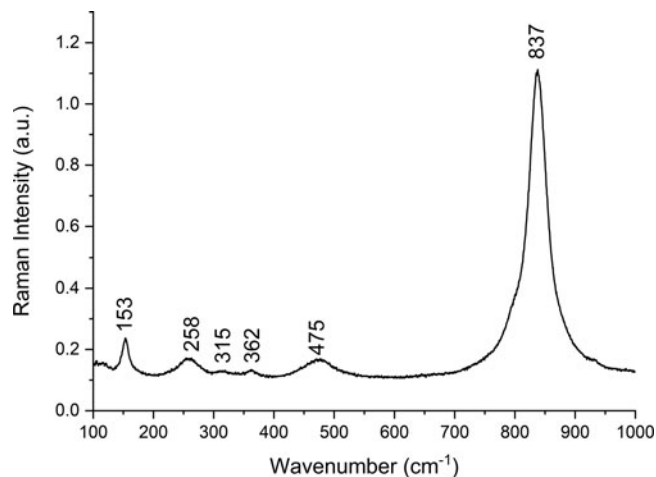


Fig. 6. Raman spectrum of medvedevite.

Table 6. Assignment of the Raman and FTIR bands for medvedevite $KMn^{2+}V_2^{5+}O_6Cl \cdot 2H_2O$.

Raman band, cm^{-1}	FTIR bands, cm^{-1}	Assignment
153		$\nu(V_2O_2)_n$
258		MnO_6 modes
315		MnO_6 modes
362		MnO_6 modes
475		$\nu_s(VOV)^{str}$
	700	$\nu(V_2O_2)$
	760	$\nu_{as}(VOV)$
	840	$\nu_{as}(VOV)$
837	890	$\nu(VO)$
	1600, 1660	$\sigma_s(H-O-H)$
	3250, 3410, 3570	O-H

str – stretch, as – antisymmetric stretch, s – symmetric stretch

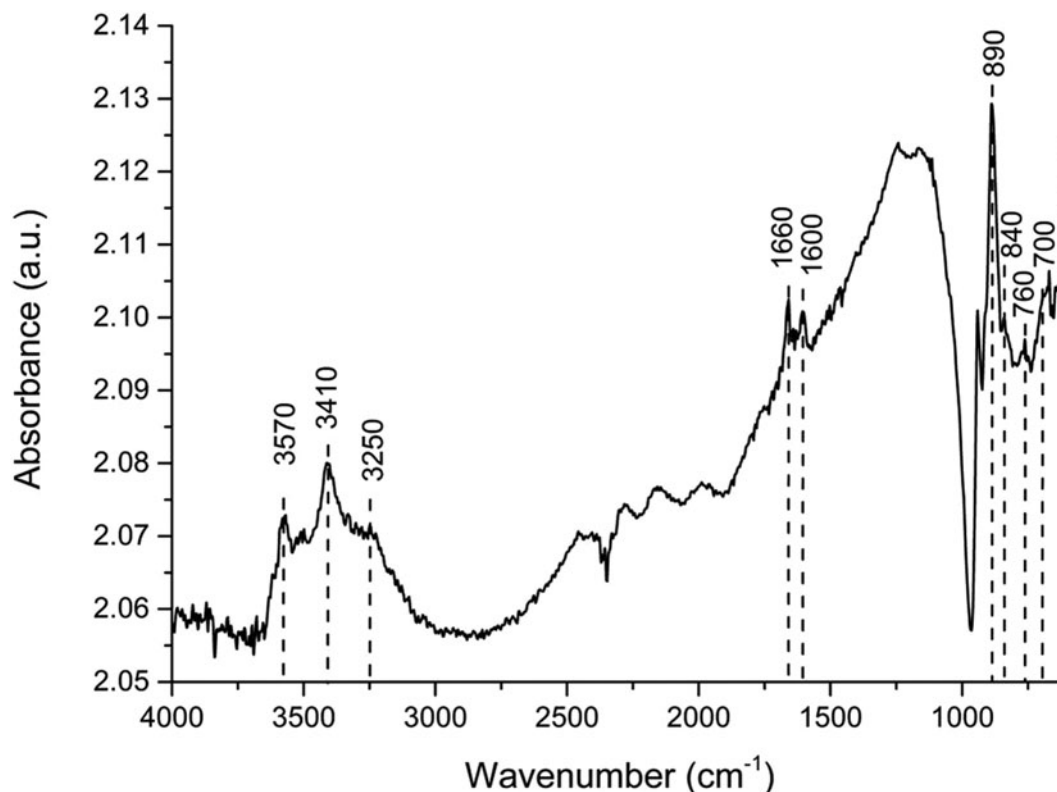


Fig. 7. FTIR spectrum of medvedevite.

According to Hawthorne and Schindler, 2008, transformer H₂O groups are “H₂O groups in which the O atoms accept only one bond from a cation (inclusive of hydrogen bonds)”. The Lewis acidity of the interstitial complex in medvedevite is 0.18 vu. The values of Lewis basicity of the structural unit and Lewis acidity of the interstitial complex agree reasonably well according to the valence-matching principle (Brown, 1981) and medvedevite is a stable structure.

Table 7. Bond-valence analysis (vu = valence units) for medvedevite.

	V1	V2	Mn1	K1	H7A	H7B	H8A	H8B	Σ
O1	0.77								2.14
O1 ⁱⁱⁱ	0.62								
O1 ^v		0.75							
O2	0.74	0.78		0.06					2.13
O2 ^{iv}		0.55							
O3		1.51							1.95
O3 ⁱⁱ			0.35						
O3 ^{vii}				0.09					
O4	1.55		0.38	0.19					2.02
O5	1.49								1.97
O5 ⁱⁱ			0.38	0.10					
O6		1.48		0.13					1.98
O6 ⁱ			0.37						
O7			0.35	0.04	0.85	0.85			2.09
O8									
O8 ^{viii}				0.04			0.88	0.88	1.80
Cl1		0.40							0.77
Cl1 ⁱⁱ				0.21					
Cl1 ^{vi}				0.16					
Σ	5.16	5.08	2.23	1.02					

Let us consider the hypothetical dehydration of the medvedevite. In the dehydration of rossite to metarossite, an equatorial bond V–O in rossite transforms to a vanadyl bond in metarossite. This change balances the bond-valence requirement that is caused during dehydration by the decreasing of the number of transformer H₂O groups. In the crystal structure of medvedevite, there are two H₂O groups: transformer and isolated (practically non-bonded). Dehydration of the isolated H₂O group will not disturb the stability of the medvedevite crystal structure according to the valence-matching principle. Dehydration of the transform H₂O group will lead to instability in the structure, due to the fact that the structure cannot respond by transformation of equatorial to vanadyl bonds because there cannot be more than two vanadyl bonds per V⁵⁺ atom (Schindler *et al.*, 2000a).

Supplementary material. To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2022.38>

Acknowledgements. This work was supported financially by the Russian Science Foundation (RSF) [grant no. 21-77-00069] and the Ministry of Science and Higher Education of the Russian Federation within the scientific tasks of the Institute of Silicate Chemistry (Russian Academy of Sciences) [project number 0081-2022-0002]. Technical support by the SPbSU X-ray Diffraction Centre is gratefully acknowledged.

Competing interests. The authors declare none

References

Ahmed F.R. and Barnes W.H. (1963) The crystal structure of rossite. *The Canadian Mineralogist*, 7, 713–726.

- Baran E.J., Cabello C.I. and Nord A.G. (1987) Raman spectra of some $M^{II}V_2O_6$ brannerite-type metavanadates. *Journal of Raman Spectroscopy*, **18**, 405–407.
- Britvin S.N., Dolivo-Dobrovolsky D.V. and Krzhizhanovskaya M.G. (2017) Software for processing the X-ray powder diffraction data obtained from the curved image plate detector of Rigaku RAXIS Rapid II diffractometer. *Proceedings of the Russian Mineralogical Society*, **146**, 104–107 [in Russian].
- Brown I.D. (1981) The bond-valence method: an empirical approach to chemical structure and bonding. Pp. 1–30 in: *Structure and Bonding in Crystals 2* (M. O'Keeffe, A. Navrotsky, editors). Academic Press, New York, USA.
- Brown I.D. and Altermatt D. (1985) Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Crystallographica*, **B41**, 244–247.
- Brugger J., Berlepsch P., Meisser N. and Armbruster T. (2003) Ansermetite, $MnV_2O_6 \cdot 4H_2O$, a new mineral species with V^{5+} in five-fold coordination from Val Ferrera, Eastern Swiss Alps. *The Canadian Mineralogist*, **41**, 1423–1431.
- Butt K.A. and Mahmood K. (1983) Munirite, naturally occurring sodium vanadium oxide hydrate, a new mineral. *Mineralogical Magazine*, **47**, 391–392.
- Dolomanov O.V., Bourhis L., Gildea R.J., Howard J.A.K. and Puschmann H. (2009) OLEX2: A complete structure solution, refinement and analysis program. *Journal of Applied Crystallography*, **42**, 339–341.
- Frost R., Erickson K.L. and Weier M.L. (2004) Hydrogen bonding in selected vanadates: a Raman and infrared spectroscopy study. *Spectrochimica Acta*, **A60**, 2419–2423.
- Hawthorne F.C. (1983) Graphical enumeration of polyhedral clusters. *Acta Crystallographica*, **A39**, 724–736.
- Hawthorne F.C. (1985) Towards a structural classification of minerals: the $^{VI}M^{IV}T_2\phi$ minerals. *American Mineralogist*, **70**, 455–473.
- Hawthorne F.C. (2015) Toward theoretical mineralogy: A bond-topological approach. *American Mineralogist*, **100**, 696–713.
- Hawthorne F.C. and Schindler M. (2008) Understanding the weakly bonded constituents in oxysalt minerals. *Zeitschrift für Kristallographie*, **223**, 41–68.
- Hughes J.M., Cureton F.E., Marty J., Gault R.A., Gunter M.E., Campana C.F., Rakovan J., Sommer A. and Brueseke M.E. (2001) Dickthomssenite, $Mg(V_2O_6) \cdot 7H_2O$, a new mineral species from the Firefly-Pigmy Mine, Utah: descriptive mineralogy and arrangement of atoms. *The Canadian Mineralogist*, **39**, 1691–1700.
- Kampf A.R., Marty J., Nash B.P., Plasil J., Kasatkin A.V. and Skoda R. (2012) Calciodelrioite, $Ca(VO_3)_2(H_2O)_4$, the Ca analogue of delrioite, $Sr(VO_3)_2(H_2O)_4$. *Mineralogical Magazine*, **76**, 2803–2817.
- Kato K. and Takayama E. (1984) Das entwaesserungsverhalten des natriumm-tavanadatdihydrats und die kristallstruktur des beta-natriumm-tavanadats. *Acta Crystallographica*, **B40**, 102–105.
- Kelsey C.H. and Barnes W.H. (1960) The crystal structure of metarossite. *Canadian Mineralogist*, **6**, 448–466.
- Levi E. and Aurbach D. (2014) Crystal chemistry and valence determinations. *Solid State Ionics*, **257**, 1–8.
- Mandarino J.A. (1981) The Gladstone–Dale relationship. IV. The compatibility concept and its application. *The Canadian Mineralogist*, **19**, 441–450.
- Pekov I.V., Zubkova N.V., Zelenski M.E., Yapaskurt V.O., Polekhovskiy Y.S., Fadeeva O.A. and Pushcharovskiy D.Y. (2013) Yaroshevskite, $Cu_9O_2(VO_4)_4Cl_2$, a new mineral from the Tolbachik volcano, Kamchatka, Russia. *Mineralogical Magazine*, **77**, 107–116.
- Pekov I.V., Koshlyakova N.N., Zubkova N.V., Lykova I.S., Britvin S.N., Yapaskurt V.O., Agakhanov A.A., Shchipalkina N.V., Turchkova A.G. and Sidorov E.G. (2018a) Fumarolic arsenates – a special type of arsenic mineralization. *European Journal of Mineralogy*, **30**, 305–322.
- Pekov I.V., Zubkova N.V., Koshlyakova N.N., Belakovskiy D.I., Vigasina M.F., Agakhanov A.A., Turchkova A.G., Britvin S.N., Sidorov E.G. and Pushcharovskiy D.Y. (2018b) Udinaite, IMA 2018-066. CNMNC Newsletter 45. *Mineralogical Magazine*, **82**, 1037–1043.
- Pekov I.V., Agakhanov A.A., Zubkova N.V., Koshlyakova N.N., Shchipalkina N.V., Sandalov F.D., Yapaskurt V.O., Turchkova A.G. and Sidorov E.G. (2020a) Oxidizing-type fumarolic systems of the Tolbachik volcano – a mineralogical and geochemical unique. *Russian Geology and Geophysics*, **61**, 675–688.
- Pekov I.V., Zubkova N.V., Yapaskurt V.O., Polekhovskiy Y.S., Britvin S.N., Turchkova A.G., Sidorov E.G. and Pushcharovskiy D.Y. (2020b) Kainotropite, $Cu_4Fe^{3+}O_2(V_2O_7)(VO_4)$, a new mineral with a complex vanadate anion from fumarolic exhalations of the Tolbachik volcano, Kamchatka, Russia. *The Canadian Mineralogist*, **58**, 155–165.
- Schindler M., Hawthorne F.C. and Baur W.H. (2000a) A crystal-chemical approach to the composition and occurrence of vanadium minerals. *The Canadian Mineralogist*, **38**, 1443–1456.
- Schindler M., Hawthorne F.C. and Baur W.H. (2000b) Crystal-chemical aspects of vanadium: polyhedral geometries, characteristic bond valences, and polymerization of (VOn) polyhedra. *Chemistry of Materials*, **12**, 1248–1259.
- Shablinskii A.P., Avdontseva M.S., Vergasova L.P., Filatov S.K., Avdontseva E.Y., Povolotskiy A.V., Moskaleva S.V., Kargopoltsev A.A. and Britvin S.N. (2022) Medvedevite, IMA 2021-082. CNMNC Newsletter 65; *European Journal of Mineralogy*, **34**, 142–148.
- Sheldrick G.M. (2015) Crystal structure refinement with SHELXL. *Acta Crystallographica*, **C71**, 3–8.
- Siidra O.I., Krivovichev S.V., Armbruster T., Filatov S.K., Pekov I.V. (2007) The crystal structure of leningradite, $PbCu_3(VO_4)_2Cl_2$. *The Canadian Mineralogist*, **45**, 445–449.
- Siidra O.I., Nazarchuk E.V., Agakhanov A.A. and Polekhovskiy Y.S. (2019a) Aleutite $[Cu_5O_2](AsO_4)(VO_4) \cdot (Cu_{0.5}\square_{0.5})Cl$, a new complex salt-inclusion mineral with Cu^{2+} substructure derived from Kagome-net. *Mineralogical Magazine*, **83**, 847–853.
- Siidra O.I., Nazarchuk E.V., Zaitsev A.N., Polekhovskiy Y.S., Wenzel T. and Spratt J. (2019b) Dokuchaevite, $Cu_8O_2(VO_4)_3Cl_3$, a new mineral with remarkably diverse Cu^{2+} mixed-ligand coordination environments. *Mineralogical Magazine*, **83**, 749–755.
- Smith M.L. (1970) Delrioite and metadelrioite from Montrose County, Colorado. *American Mineralogist*, **55**, 185–200.
- Starova G.L., Krivovichev S.V., Fundamenskiy V.S. and Filatov S.K. (1997) The crystal structure of averievite, $Cu_5O_2(VO_4)_2 \cdot nMX$: comparison with related compounds. *Mineralogical Magazine*, **61**, 441–446.
- Thompson M.E. and Sherwood A.M. (1959) Delrioite, a new calcium strontium vanadate from Colorado. *American Mineralogist*, **44**, 261–264.
- Vergasova L.P. and Filatov S.K. (2012) New mineral species in products of fumarole activity of Great Tolbachik fissure eruption. *Journal of Volcanology and Seismology*, **6**, 281–289.
- Vergasova L.P. and Filatov S.K. (2016) A study of volcanogenic exhalation mineralization. *Journal of Volcanology and Seismology*, **10**, 71–85.
- Vergasova L.P., Filatov S.K., Semenov T.F. and Anan'ev V.V. (1990) Leningradite $PbCu_3(VO_4)_2Cl_2$, a new mineral from volcanic exhalations. *Doklady Akademii Nauk*, **310**, 157–160 [in Russian].
- Vergasova L.P., Starova G.L., Filatov S.K. and Anan'ev V.V. (1998) Averievite $Cu_5(VO_4)_2O_2 \cdot nMX$ – a new mineral of volcanic exhalations. *Doklady Akademii Nauk*, **359**, 804–807 [in Russian].
- Vergasova L.P., Filatov S.K., Moskaleva S.V., Nazarova M.A., and Shablinskii A.P. (2022) Post-eruptive Activity of the Third Scoria Cone of the Northern Breakthrough of the Great Fissure Tolbachik Eruption (Kamchatka, 1975–1976). *Journal of Volcanology and Seismology*, **3**, 1–15.
- Yao G., Ren Z. and Liu P. (2018) Effect of Ca substitution on microwave dielectric properties of BaV_2O_6 ceramics. *Journal of Electroceramics*, **40**, 144–149.
- Zelenski M.E., Zubkova N.V., Pekov I.V., Boldyreva M.M., Pushcharovskiy D.Yu., Nekrasov A.N. (2011) Pseudovolonsite, $Cu_3(VO_4)_2$, a new mineral species from the Tolbachik volcano, Kamchatka Peninsula, Russia. *European Journal of Mineralogy*, **23**, 475–481.