Unique thallium mineralization in the fumaroles of Tolbachik volcano, Kamchatka Peninsula, Russia. III. Evdokimovite, $TI_4(VO)_3(SO_4)_5(H_2O)_5$

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ABSTRACT

Evdokimovite, ideally $Tl_4(VO)_3(SO_4)_5(H_2O)_5$, was found in a fumarole of the 1st cinder cone of the North Breach of the Great Fissure Tolbachik volcano eruption of 1975-1976, Kamchatka Peninsula, Russia. Evdokimovite occurs as thin, colourless needles up to 0.09 mm long associated with shcherbinaite, pauflerite, bobjonesite, markhininite, karpovite and microcrystalline Mg, Al, Fe and Na sulfates. Evdokimovite is monoclinic, $P2_1/n$, a = 6.2958(14), b = 10.110(2), c = 39.426(11) Å, $\beta =$ 90.347(6)°, V = 2509.4(10) Å³ and Z = 4 (from single-crystal diffraction data). The eight strongest lines of the powder X-ray diffraction pattern are (I/d/hkl): 57/9.793/011, 100/8.014/013, 26/6.580/006, 19/ 4.011/026, 29/3.621/118, 44/3.522/125, 19/3.010/036, 21/2.974/212. Chemical composition determined by the electron microprobe analysis is (wt.%): Tl_2O 55.40, VO_2 14.92, SO_3 25.83, H_2O 5.75, total 101.90. The empirical formula for evdokimovite calculated on the basis of (TI + V + S) =12 a.p.f.u. is $Tl_{4,10}V_{2,83}S_{5,07}H_{10,00}O_{27,94}$. The simplified formula is $Tl_4(VO)_3(SO_4)_5(H_2O)_5$. The crystal structure was solved by direct methods and refined to $R_1 = 0.11$ on the basis of 3660 independent observed reflections. $V^{4+}O_6$ octahedra and SO_4 tetrahedra share common corners to form two types of vanadyl-sulfate chains, $[(VO)(H_2O)_2(SO_4)_2]^{2-}$ and $[(VO)_2(H_2O)_3(SO_4)_3]^{2-}$. Thallium atoms are located in between the chains. The structure can be described as a stacking of layers of two types, A and *B*. The *A* layer contains $[(VO)_2(H_2O)_3(SO_4)_3]^2$ chains and the Tl2 and Tl3 atoms, whereas the *B* layer contains $[(VO)(H_2O)_2(SO_4)_2]^2$ chains and the Tl1 atoms. Stacking of the layers can be described as $\dots A'^*BAA'B^*A^*\dots$, where A and A' denote A layers with opposite orientations of the $[(VO)_2(H_2O)_3(SO_4)_3]^{2-}$ chains, and the A* and B* layers are rotated by 180° relative to the A and B layers, respectively. $[(VO)_2(H_2O)_3(SO_4)_3]^{2-}$ chains are modulated and are arranged to form elliptical tunnels hosting disordered Tl(4), Tl(4A) and Tl(4B) sites. The new mineral is named in honour of Professor Mikhail Dmitrievich Evdokimov (1940–2010), formerly of the Department of Mineralogy, St Petersburg State University, for his contributions to mineralogy and petrology, and especially for teaching mineralogy to several generations of students at the University. Evdokimovite is the most complex V⁴⁺ sulfate known to date with structural information amounting to 1130 bits per unit cell, which places evdokimovite among minerals with the complexity of the vesuvianite group.

* E-mail: o.siidra@spbu.ru DOI: 10.1180/minmag.2014.078.7.14 **Keywords:** evdokimovite, new mineral, thallium, vanadium, vanadyl ion, sulfate, lone electron pair, Tolbachik volcano, structural complexity.

Introduction

EVDOKIMOVITE is one of three new minerals described from the unusual Tl(I)-rich sulfate mineral assemblage of the Tolbachik volcano, Kamchatka Peninsula, Russia (Fedotov and Markhinin, 1983). During the investigation of markhininite (Siidra et al., 2014a) samples, on the basis of semi-quantitative scanning electron microscopy (SEM) energy dispersive spectroscopy analysis, two new species were found: evdokimovite and karpovite (Siidra et al., 2014b). Evdokimovite was named in honour of Professor Mikhail Dmitrievich Evdokimov (1940-2010). Mikhail Evdokimov worked at the Department of Mineralogy, St Petersburg State University, Russia, from the 1960s. Besides his many scientific achievements he was an outstanding lecturer in mineralogy and taught several generations of mineralogists now working in different fields of science and industry. Evdokimov specialized in the mineralogy and petrology of alkaline intrusive metasomatic rocks. Both the mineral and the mineral name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (proposal IMA 2013-041, Siidra, et al., 2013). Type material is deposited in the Mineralogical Museum, St

Petersburg State University, St Petersburg, Russia, catalogue number 1/19542.

Occurrence and physical properties

Evdokimovite was found in a sample from the first cinder cone of the North breach of the Great Fissure Tolbachik eruption (GFTE), Kamchatka Peninsula, Russia, together with markhininite, $TlBi(SO_4)_2$ and karpovite, $Tl_2VO(SO_4)_2(H_2O)$ (Siidra et al., 2014a,b). Other associated minerals are pauflerite, β -(V⁴⁺O(SO₄)) (Fig. 1), bobjonesite, $V^{4+}O(SO_4)(H_2O)_3$ and scherbinaite, $V_2^{5+}O_5$. The mineral occurs as thin, colourless needles up to 0.09 mm long (Fig.2). Evdokimovite has a white streak and an adamantine lustre. It is brittle with no cleavage or parting observed and a conchoidal fracture. The Mohs hardness of evdokimovite is $\sim 2\frac{1}{2}$ and the average VHN₁₀₀ hardness is 92.3 kg mm⁻². The calculated density for the ideal formula of $Tl_4(VO)_3(SO_4)_5(H_2O)_5$ is 4.20 g cm^{-3} . No twinning has been observed.

The mineral is nonmetallic, but has high refraction indices typical of Tl oxysalts and has been studied using the methods common for metallic minerals to avoid using toxic RI liquids. In reflected light the mineral is light grey with beige tints, with weak bireflectance and no pleochroism,



FIG. 1. Abundant white needles with adamantine lustre of evdokimovite with pauflerite (green) and bluish aggregates of karpovite and bobjonesite. Field of view is 4 mm.



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FIG. 2. SEM image of prismatic crystals of evdokimovite with tabular crystals of markhininite.

TABLE 1. Reflectance values of an unoriented section of evdokimovite free of internal reflections on a measured area of 10 μ m \times 10 μ m (SiC standard, measured in air).

λ (nm)	R_{\max} (%)	R_{\min} (%)
400	7.42	7.23
420	7.34	7.15
440	7.26	7.08
460	7.19	6.99
470	7.16	6.95
480	7.12	6.91
500	7.04	6.84
520	6.95	6.78
540	6.89	6.72
546	6.87	6.70
560	6.83	6.66
580	6.78	6.60
589	6.75	6.58
600	6.71	6.54
620	6.65	6.47
640	6.60	6.43
650	6.58	6.40
660	6.56	6.38
680	6.52	6.34
700	6.47	6.29

Note: The values for wavelengths (λ) recommended by the IMA Commission on Ore Microscopy (COM) are given in bold.

while any anisotropy is masked by abundant greenish-grey internal reflections. Reflectance measurements were made using a SiC standard in air in the range 400–700 nm (Table 1).

Chemical composition

Chemical analyses (30) were performed using a Camscan-4DV electron microscope and an

AN-10000 semiconductor spectrometer operating at 20 kV and 1 nA at the Radium Institute. St Petersburg. TlLa, VKa and SKa, were used as analytical lines. The signal for $TIM\alpha$ was subtracted to get the correct chemical formula because of partial overlap with the SK α line. All calculations were made using AF4/FLS software. Fe, Bi, As, Cu, P and Si were sought but were below detection limits. No other elements were detected. H₂O was not determined directly because of the paucity of the material available but was calculated by stoichiometry from the results of the crystal-structure analysis. Microprobe analysis of evdokimovite crystals revealed some difficulties, due to the fact that the mineral contains five water molecules per formula unit, which obviously affected the quality of the data and the ratios of elements. Analytical data are given in Table 2. The empirical formula for evdokimovite calculated on the basis of (Tl + V + S) = 12 atoms per formula unit is Tl_{4.10}V_{2.83}S_{5.07}H_{10.00}O_{27.94}. The simplified formula is $Tl_4(VO)_3(SO_4)_5(H_2O)_5$, which requires Tl₂O 54.29, SO₃ 25.58, VO₂ 14.38, H₂O 5.75, total 100.00 wt.%.

Powder X-ray diffraction data

Powder X-ray diffraction (XRD) data for evdokimovite were obtained using a Stoe IPDS II diffractometer at the Department of Crystallography, St Petersburg State University, Russia, after crushing the crystal fragment used for the single-crystal analysis. Data (in Å for MoK α) are given in Table 3. The data were refined in space group $P2_1/n$, a = 6.292(9), b = 10.103(9), c =39.43(2) Å, $\beta = 90.4(1)^\circ$, V = 2506(3) Å³ and Z = 4. The eight strongest lines of the powder XRD pattern are (I/d/hkl): 57/9.793/011, 100/ 8.014/013, 26/6.580/006, 19/4.011/026, 29/3.621/ 118, 44/3.522/125, 19/3.010/036, 21/2.974/212.

TABLE 2. Chemical composition (wt.%) of evdokimovite.

Constituent	Wt.%	Range	SD	Probe standard
Tl ₂ O	55.40	54.2-56.01	0.07	TlI
$V\tilde{O}_2$	14.92	12.09-15.62	0.03	Vanadinite
SO ₃	25.83	24.39-27.03	0.08	Pyrite
H ₂ O*	5.75			5
Total	101.90			

* Calculated on the basis of crystal-structure data.

I _{rel}	$d_{\rm obs}$ (Å)	d_{calc} (Å)	h	k	l
11	19.71	19.71	0	0	2
57	9.793	9.793	0	1	1
100	8.014	8.013	0	1	3
26	6.580	6.571	0	0	6
11	6.218	6.218	0	1	5
5	5.693	5.691	1	0	3
15	5.292	5.292	1	1	1
9	5.167	5.165	1	1	2
	4.905	4.905	l	0	5
9	4.259	4.257	0	2	2
0	4.011	4.007	1	2	0
0 5	3.942	3.942	1	2 1	7
15	3.613	3.665	1	2	$\frac{i}{4}$
29	3.621	3.614	1	1	8
44	3.522	3.5203	1	2	5
7	3.320	3.3794	1	1	9
13	3.313	3.322	0	3	2
18	3.264	3.264	0	3	3
7	3.160	3.165	1	1	10
9	3.123	3.123	1	0	11
12	3.108	3.107	1	0	11
19	3.010	2.999	0	3	6
21	2.974	2.974	2	1	2
11	2.925	2.925	l	2	9
8	2.900	2.900	1	3	3
18	2.893	2.890	1	3	3 12
5	2.801	2.803	0	3	8
9	2.782	2.782	1	3	ē
18	2.660	2.660	2	0	8
9	2.582	2.582	2	2	4
11	2.527	2.527	2	2	5
15	2.480	2.480	2	2	6
12	2.457	2.453	2	0	10
9	2.397	2.408	1	2	13
10	2.329	2.329	1	4	2
	2.297	2.297	2	3	
/	2.287	2.287	1	2	14
24 17	2.270	2.270	2	∠ ⊿	9 Q
8	2.200	2.249	0	2	0 16
4	2.174	2.174	2	3	6
10	2.161	2.161	$\tilde{0}$	3	14
4	2.111	2.108	0	2	17
15	1.985	1.974	1	0	ī9
11	1.960	1.960	2	4	2
9	1.847	1.847	1	5	6
8	1.833	1.833	1	2	19
5	1.690	1.690	0	1	23
4	1.612	1.612	2	4	14
5 5	1.323	1.323	4	2	14 ō
5 4	1.212	1.212	5 1	1	9 36
+ 4	1.134	1.134	1 4	5	20
6	0.982	0.982	5	5	16
3	0.918	0.917	5	1	29
3	0.813	0.813	5	2	36

TABLE 3. Powder XRD data for evdokimovite. The eight strongest powder lines are given in bold.

Crystal structure

Experimental

The small size of acicular crystals of evdokimovite and their intimate intergrowths made a highquality crystal-structure study of the mineral rather difficult. A needle measuring $0.05 \text{ mm} \times 0.01 \text{ mm} \times 0.008 \text{ mm}$ was mounted on a Bruker APEX II DUO X-ray diffractometer equipped with a micro-focus X-ray tube operated with MoKa radiation at 50 kV and 40 mA. Data were integrated and corrected for absorption with a multi-scan model using the Bruker programs APEX and SADABS. More than a hemisphere of data was collected with frame widths of 0.3° in ω and with 120 s counting for each frame. The structure was solved by direct methods in space group $P2_1/n$ and refined to $R_1 = 0.11$ for 3660 unique observed reflections (Table 4). Positions of the H atoms could not be localized. Attempts to refine atom positions of non-Tl atoms in an anisotropic approximation were unsuccessful. Due to the poor quality of XRD data for evdokimovite crystals, the quality of the crystal structure refinement is rather low and does not allow detailed discussion of structural parameters and bond-valence calculations. Atom coordinates, displacement parameters and selected bond lengths are given in Tables 5, 6 and 7.

TABLE 4. Crystallographic data and refinement parameters for evdokimovite.

Crystal size (mm)	$0.05 \times 0.01 \times 0.008$
Space group	$P2_1/n$
a (Å)	6.2958(14)
b (Å)	10.110(2)
c (Å)	39.426(11)
β (°)	90.347(6)
$V(A^3)$	2509.4(10)
$\mu (mm^{-1})$	27.189
D_{calc} (g cm ⁻³)	4.20
Radiation wavelength (Å)	0.71073 (MoKα)
θ range (deg.)	1.03-25.15
Total Ref.	12,111
Unique Ref.	4451
Unique $F \ge 4\sigma(F)$	3660
Rint	0.07
R_1	0.11
R_1 (all data)	0.13
WR_2	0.26
Gof	1.158
$\rho_{\text{max,min}}$ (e Å ⁻³)	+4.204/-3.144

TI MINERALIZATION, TOLBACHIK VOLCANO: KARPOVITE, TI₂VO(SO₄)₂(H₂O)

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Atom	x/a	y/b	z/c	$U_{ m eq}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	T11	0.5525(3)	0.13654(19)	0.20117(5)	0.0281(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	T12	0.2937(3)	0.76251(19)	0.13287(5)	0.0315(5)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	T13	0.9115(3)	0.4624(2)	0.13815(5)	0.0341(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Tl4*	0.2703(12)	-0.0970(4)	0.03510(10)	0.0865(18)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Tl4A**	0.062(2)	-0.0508(14)	0.0161(3)	0.044(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Tl4B***	0.429(4)	-0.0568(19)	0.0179(6)	0.056(6)
$\begin{array}{ccccccc} \mathbb{V}2 & 0.7570(10) & 0.0665(6) & 0.10279(16) & 0.0114(14) \\ \mathbb{V}3 & 0.2353(10) & 0.3305(6) & 0.05437(16) & 0.0083(13) \\ \mathbb{S}1 & 0.2505(14) & 0.1151(9) & 0.1128(2) & 0.0133(19) \\ \mathbb{S}2 & 0.4681(17) & 0.4781(11) & 0.1899(3) & 0.018(2) \\ \mathbb{S}3 & 0.7508(15) & 0.2947(10) & 0.0462(2) & 0.013(2) \\ \mathbb{S}4 & 0.5346(15) & 0.2762(10) & 0.2854(2) & 0.014(2) \\ \mathbb{S}5 & 0.7589(18) & -0.2530(12) & 0.0714(3) & 0.026(2) \\ \mathbb{O}1 & 0.504(4) & 0.189(3) & 0.3157(6) & 0.009(5) \\ \mathbb{O}2 & 0.072(4) & 0.048(3) & 0.0949(7) & 0.017(6) \\ \mathbb{O}3 & 0.758(5) & -0.077(3) & 0.1396(8) & 0.025(7) \\ \mathbb{H}_2 05 & 0.042(5) & 0.164(3) & 0.2163(8) & 0.031(8) \\ \mathbb{O}6 & 0.938(4) & 0.369(3) & 0.0611(6) & 0.012(5) \\ \mathbb{O}7 & -0.431(4) & 0.411(3) & 0.2981(6) & 0.013(6) \\ \mathbb{O}8 & 0.723(5) & 0.230(3) & 0.2658(8) & 0.028(7) \\ \mathbb{H}_2 09 & 0.251(5) & 0.435(3) & 0.0093(8) & 0.026(7) \\ \mathbb{O}10 & 0.247(5) & 0.199(3) & 0.0336(7) & 0.019(6) \\ \mathbb{O}11 & 0.760(5) & 0.187(3) & 0.1292(8) & 0.026(7) \\ \mathbb{O}12 & 0.753(4) & 0.147(3) & 0.0568(7) & 0.014(6) \\ \mathbb{O}13 & 0.744(4) & -0.110(3) & 0.0707(7) & 0.013(6) \\ \mathbb{H}_2 014 & 0.996(4) & 0.421(3) & 0.2407(7) & 0.018(6) \\ \mathbb{O}15 & 0.565(5) & 0.388(3) & 0.1881(8) & 0.026(7) \\ \mathbb{O}16 & 0.292(5) & 0.388(3) & 0.1881(8) & 0.026(7) \\ \mathbb{O}17 & 0.242(5) & 0.110(3) & 0.1940(7) & 0.021(7) \\ \mathbb{O}18 & 0.447(5) & -0.173(3) & 0.1940(7) & 0.021(7) \\ \mathbb{O}18 & 0.447(5) & -0.173(3) & 0.1940(7) & 0.022(7) \\ \mathbb{O}19 & 0.446(5) & 0.047(3) & 0.1009(7) & 0.023(7) \\ \mathbb{H}_2 020 & 0.252(5) & 0.386(3) & 0.0736(8) & 0.026(7) \\ \mathbb{O}22 & 0.261(5) & 0.259(3) & 0.1022(7) & 0.022(7) \\ \mathbb{O}23 & 0.770(6) & -0.296(4) & 0.1881(8) & 0.026(7) \\ \mathbb{O}24 & 0.430(5) & 0.555(3) & 0.1184(8) & 0.027(7) \\ \mathbb{O}25 & 0.482(5) & 0.552(3) & 0.1584(8) & 0.027(7) \\ \mathbb{O}26 & 0.664(5) & 0.401(3) & 0.1960(7) & 0.023(7) \\ \mathbb{O}28 & 0.924(11) & -0.287(7) & 0.0515(16) & 0.11(2) \\ \end{array}$	V1	0.0387(11)	0.2572(7)	0.26966(17)	0.0142(14)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V2	0.7570(10)	0.0665(6)	0.10279(16)	0.0114(14)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V3	0.2535(10)	0.3305(6)	0.05437(16)	0.0083(13)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S1	0.2505(14)	0.1151(9)	0.1128(2)	0.0103(19)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S2	0.4681(17)	0.4781(11)	0.1899(3)	0.018(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S3	0.7508(15)	0.2947(10)	0.0462(2)	0.013(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	S4	0.5346(15)	0.2762(10)	0.2854(2)	0.014(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S5	0.7589(18)	-0.2530(12)	0.0714(3)	0.026(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	01	0.504(4)	0.189(3)	0.3157(6)	0.009(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O2	0.072(4)	0.048(3)	0.0949(7)	0.017(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O3	0.758(5)	0.304(3)	0.0096(7)	0.019(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H ₂ O4	0.756(5)	-0.077(3)	0.1396(8)	0.025(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H ₂ O5	0.042(5)	0.164(3)	0.2163(8)	0.031(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O6	0.938(4)	0.369(3)	0.0611(6)	0.012(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O7	-0.431(4)	0.411(3)	0.2981(6)	0.013(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O8	0.723(5)	0.230(3)	0.2658(8)	0.028(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H ₂ O9	0.251(5)	0.435(3)	0.0093(8)	0.026(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O10	0.247(5)	0.199(3)	0.0336(7)	0.019(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	011	0.760(5)	0.187(3)	0.1292(8)	0.026(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O12	0.753(4)	0.147(3)	0.0568(7)	0.014(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	013	0.744(4)	-0.110(3)	0.0707(7)	0.013(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H ₂ O14	0.996(4)	0.421(3)	0.2407(7)	0.018(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	015	0.565(5)	0.367(3)	0.0621(7)	0.024(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O16	0.292(5)	0.388(3)	0.1881(8)	0.026(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O17	0.242(5)	0.110(3)	0.1487(7)	0.020(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O18	0.447(5)	-0.173(3)	0.1940(7)	0.021(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O19	0.446(5)	0.047(3)	0.1009(7)	0.023(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H ₂ O20	0.252(5)	0.536(3)	0.0736(8)	0.026(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O21	0.359(4)	0.271(3)	0.2612(7)	0.020(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O22	0.261(5)	0.259(3)	0.1022(7)	0.022(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O23	0.770(6)	-0.296(4)	0.1088(10)	0.047(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O24	0.430(5)	0.565(3)	0.2194(7)	0.023(7)
O260.664(5)0.401(3)0.1960(7)0.023(7)O270.577(8)-0.314(5)0.0553(12)0.066(13)O280.924(11)-0.287(7)0.0515(16)0.11(2)	O25	0.482(5)	0.552(3)	0.1584(8)	0.027(7)
O270.577(8)-0.314(5)0.0553(12)0.066(13)O280.924(11)-0.287(7)0.0515(16)0.11(2)	O26	0.664(5)	0.401(3)	0.1960(7)	0.023(7)
O28 0.924(11) -0.287(7) 0.0515(16) 0.11(2)	O27	0.577(8)	-0.314(5)	0.0553(12)	0.066(13)
	O28	0.924(11)	-0.287(7)	0.0515(16)	0.11(2)

TABLE 5. Atom coordinates and isotropic displacement parameters ($Å^2$) for evdokimovite.

Site Occupancy Factors (SOF): * SOF = 0.70(3), **SOF = 0.17(3), ***SOF = 0.13(3).

Cation coordination

The structure of evdokimovite contains six symmetrically independent TI^+ sites, three V^{4+} sites and five S^{6+} sites. Tl4, Tl4A and Tl4B sites are occupied partly and have a total refined occupancy of 1. Three different coordination environments are observed for the Tl1, Tl2 and

Tl3 atoms (Fig. 3), if all Tl–O bonds <3.5 Å are taken into consideration. The Tl1 site is coordinated by twelve O atoms in a rather symmetrical environment, whereas the Tl2 and Tl3 sites are coordinated by eight and nine O atoms, respectively, and display more distorted configurations. The partially occupied Tl4 site has a sevenfold coordination. Almost all Tl–O bonds

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
T11	0.0258(9)	0.0285(10)	0.0298(10)	-0.0038(8)	-0.0038(8)	0.0023(8)
T12	0.0386(11)	0.0288(10)	0.0271(10)	0.0033(8)	-0.0036(8)	0.0001(9)
T13	0.0424(12)	0.0287(10)	0.0315(11)	0.0003(9)	0.0092(9)	-0.0054(9)
T14*	0.191(6)	0.0260(19)	0.042(2)	-0.0050(16)	-0.005(3)	-0.002(3)
Tl4A**	0.035(7)	0.043(7)	0.054(8)	-0.020(6)	0.009(6)	-0.004(6)
Tl4B***	0.065(13)	0.034(10)	0.069(13)	-0.005(10)	-0.055(11)	0.006(9)

TABLE 6. Anisotropic displacement parameters ($Å^2$) for Tl atoms in the crystal structure of evdokimovite.

* SOF = 0.70(3), **SOF = 0.17(3), ***SOF = 0.13(3).

shorter than 3 Å (except the Tl1–O8 bond) are to O atoms that either belong to the vanadyl ions or are terminal atoms of SO_4 tetrahedra.

The V sites are each surrounded by six O atoms to form distorted $V^{4+}O_6$ octahedra. The O4, O5, O9, O14 and O20 sites belong to the H₂O molecules, so that V-centred octahedra have the compositions V1O₄(H₂O)₂, V2O₅(H₂O) and V3O₄(H₂O)₂ (Figs 4 and 5). In each octahedron, there is one short VO vanadyl bond (1.60, 1.61 and 1.56 Å for V1, V2, and V3, respectively) opposite to one long V–H₂O bond (2.31, 2.19 and 2.21 Å for V1, V2 and V3, respectively). The coordination of V⁴⁺ in evdokimovite is similar to that in the structure of karpovite (Siidra *et al.*, 2014*b*) and is typical for vanadium oxysalts with V^{4+} in [1+4+1] coordination (Schindler *et al.*, 2000).

All symmetrically-independent S^{6+} cations are tetrahedrally coordinated by the O atoms.

Structure description

In the structure of evdokimovite, $V^{4+}O_6$ octahedra and SO₄ tetrahedra share common corners to form two types of vanadyl-sulfate chains, $[(VO)(H_2O)_2(SO_4)_2]^{2-}$ (Fig. 4) and $[(VO)_2(H_2O)_3(SO_4)_3]^{2-}$ (Fig. 5). Thallium atoms are located between the vanadyl sulfate chains (Fig. 6*a*). The structure of evdokimovite can be described as a stacking of layers of two types, *A* and *B*. The *A* layer (Fig. 6*a*) contains



FIG. 3. Coordination of Tl^+ cations in the structure of evdokimovite (upper). Coordination polyhedra of the T11, T12 and T13 atoms (CN = coordination number) (lower).

Tl1-O26	2.78(3)	V1-O18	1.60(3)
Tl1-017	2.85(3)	V1-O24	2.00(3)
T11-08	2.92(3)	V1-08	2.01(3)
T11 - 021	3,00(3)	$V_{1} - H_{2}O_{14}$	2.03(3)
T11 - 0.16	3.00(3)	V1 - 021	2.05(3)
T11 U O5	2.15(2)	V1 U05	2.03(3)
$111 - 11_{2}03$	3.13(3)	v1-H2O3	2.31(3)
T11_U_014	3.17(3)	V2 011	1(1(2))
$H_{11} - H_{2} O I 4$	3.18(3)	V2-011	1.01(3)
III-018	3.21(3)	V2-019	1.9/(3)
$H_{2}O_{2}$	3.28(3)	V2-012	1.99(3)
111-07	3.29(3)	V2-02	2.02(3)
$Tl1-H_2O4$	3.50(3)	$V2-H_2O4$	2.05(3)
		V2-013	2.19(3)
T12-O25	2.64(3)		
Tl2-O18	2.67(3)	V3-O10	1.56(3)
Tl2-O1	2.87(2)	V3-O15	2.02(3)
Tl2-O23	3.21(4)	V3-O22	2.02(3)
Tl2-H ₂ O20	3.28(3)	V3-O6	2.05(3)
Tl2-019	3.28(3)	V3-H ₂ O9	2.07(3)
T12-H ₂ O4	3.34(3)	$V_{3}-H_{2}O_{2}O_{2}O_{2}O_{2}O_{2}O_{2}O_{2}O$	2.21(3)
$T_{12} - 0.23$	3 47(4)		()
112 020	5117(1)	S1-017	1.42(3)
T13 - 0.26	2.84(3)	S1-02	1.48(3)
T13 - 023	2.01(3) 2 84(4)	S1-019	1 49(3)
TI3_011	2.01(1) 2.96(3)	S1-022	1.19(3) 1.51(3)
T13 - 0.025	2.96(3)	51 022	1.51(5)
T13 - 023 T12 - 01	2.90(3)	\$2 016	1 44(2)
T13-01	2.97(3) 2.18(2)	S2-010 S2 025	1.44(3) 1.45(3)
T13-010	3.18(3)	S2-025	1.43(3)
T13-06	3.18(3)	S2-026	1.4/(3)
T13-022	3.33(3)	82-024	1.48(3)
$H_{3}-H_{2}O_{2}O_{2}O_{2}O_{2}O_{2}O_{2}O_{2}O$	3.42(3)	62 62	1 44(2)
		\$3-03	1.44(3)
TI4-TI4B	1.30(3)	S3-O6	1.51(3)
Tl4-Tl4A	1.58(1)	S3-O15	1.52(3)
		S3-O12	1.55(3)
Tl4-O3	2.74(3)		
Tl4-028	2.98(7)	S4-O21	1.46(3)
Tl4-O10	3.00(3)	S4-O7	1.47(3)
Tl4-027	3.02(5)	S4-O1	1.50(3)
Tl4-O2	3.05(3)	S4-O8	1.50(3)
Tl4-019	3.17(3)		. /
T14-013	3.29(3)	S5-O28	1.35(7)
		\$5-027	1.44(5)
		S5-013	1 45(3)
		85-023	1.13(3) 1.54(4)
		55 025	1.54(4)

TABLE 7. Selected interatomic distances (Å) in the crystal structure of evdokimovite.

 $[(VO)_2(H_2O)_3(SO_4)_3]^{2-}$ chains, and the Tl2 and Tl3 atoms, whereas the *B* layer contains $[(VO)(H_2O)_2(SO_4)_2]^{2-}$ chains together with the Tl1 atoms. $[(VO)(H_2O)_2(SO_4)_2]^{2-}$ chains are stacked in a wave-like manner with sulfate tetrahedra pointing either up or down relative to the plane of the *B* layer. All $[(VO)_2(H_2O)_3(SO_4)_3]^{2-}$ and $[(VO)(H_2O)_2(SO_4)_2]^{2-}$ chains

have the same orientation within one *A* and *B* layer, respectively. Stacking of the layers can be described as ...A'*BAA'B*A*..., where *A* and *A'* denote *A* layers with opposite orientations of the $[(VO)_2(H_2O)_3(SO_4)_3]^{2-}$ chains and the *A** and *B** layers are rotated by 180° relative to the *A* and *B* layers, respectively. $[(VO)_2(H_2O)_3(SO_4)_3]^{2-}$ chains are modulated and are arranged to form



FIG. 4. Polyhedral, ball-and-stick and graph representations of the $[(VO)(H_2O)_2(SO_4)_2]^{2-}$ chains in evdokimovite. VO₄(H₂O)₂ and VO₅H₂O octahedra = green, SO₄ tetrahedra = yellow; V, S O and H₂O are shown as grey, yellow, red and blue spheres, respectively.

elliptical tunnels hosting the disordered TI(4), TI(4A) and TI(4B) sites (Fig. 6*b*).

Discussion

The crystal structure of evdokimovite is unique among known oxysalt minerals and synthetic compounds (Krivovichev, 2009) and is based upon heteropolyhedral chains of two topologically different types (Figs 4 and 5) linked by Tl atoms and H bonds. In order to investigate the topological nature of the $[(VO)(H_2O)_2(SO_4)_2]^{2-1}$ and $[(VO)_2(H_2O)_3(SO_4)_3]^{2-}$ chains their graph representations can be examined (Figs 4 and 5), where each node represents either a VO_6 octahedron (black node) or an SO₄ tetrahedron (white node). Two nodes are connected by an edge if the corresponding polyhedra share at least one common atom. The structure of the $[(VO)_2(H_2O)_3SO_4)_3]^{2-}$ chain is unique and has not been observed previously in any onedimensional (chain) octahedral-tetrahedral oxysalt structure. However, double-strand chains with no additional tetrahedra attached were described recently in kapundaite, $(Na,Ca)_2Fe_4^{3+}$ $(PO_4)_4(OH)_3$ ·5H₂O (Mills *et al.*, 2010). The

 $[(VO)(H_2O)_2(SO_4)_2]^{2-}$ chain is similar to the V⁵⁺ phosphate chains in synthetic Ba₂(VO₂)(PO₄) (HPO₄)(H₂O) (Bircsak and Harrison, 1998). The structure of evdokimovite is centrosymmetric, despite the fact that both $[(VO)(H_2O)_2(SO_4)_2]^{2-}$ and $[(VO)_2(H_2O)_3(SO_4)_3]^{2-}$ chains are asymmetric. Figure 7 provides graph representations and indicates close structural relationships of the heteropolyhedral units observed in markhininite (Siidra *et al.*, 2014*a*), karpovite (Siidra *et al.*, 2014*b*) and evdokimovite.

The structure of evdokimovite is strongly controlled by the stereochemical activity of the so-called 'lone electron pairs' on the Tl⁺ cations. The modulated character of the $[(VO)_2(H_2O)_3 SO_4)_3]^{2-}$ chains and the wave-like arrangement of the $[(VO)(H_2O)_2(SO_4)_2]^{2-}$ chains is obviously influenced by the large Tl⁺ cations with strongly asymmetric coordination environments. Table 8 provides information on ECC_v (volume eccentricity) parameters (Makovicky and Balić-Žunić, 1998) calculated with the computer program *IVTON* v.2 (Balić-Žunić and Vickovic, 1996) for markhininite (Siidra *et al.*, 2014*a*), karpovite (Siidra *et al.*, 2014*b*) and evdokimovite (with the exception of the low occupancy Tl4, Tl4A and



FIG. 5. Polyhedral, ball-and-stick and graph representations of the $[(VO)_2(H_2O)_3SO_4)_3]^{2-}$ chains in evdokimovite. Legend as in Fig.4.

Mineral	Site	CN	ECC _{vol}	$V_{polyhedron}$ (Å ³)
Markhininite TIBi(SQ ₄) ₂	T11	14	0.0	85.55
1101(004)2	T12	14	0.0	82.47
	T13	14	0.0	84.78
	T14	14	0.0	80.48
Karpovite $T_{1}VO(SO_{1})$ (H ₂ O)	T11	10	0.1274	54.96
112 (0(504)2(1120)	T12	9	0.1791	45.02
Evdokimovite		10	0.40.50	-1.10
$TL(VO)_{2}(SO_{1})_{2}(H_{2}O)_{2}$	TH	12	0.1959	/1.10
114(*0)3(004)5(1120)5	T12	8	0.4222	41.91
	T13	9	0.2487	55.10

TABLE 8. Selected polyhedral parameters for Tl atoms in markhininite, karpovite and evdokimovite.

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FIG. 6. General projection of the crystal structure of evdokimovite along the *a* axis (*a*) and disordered Tl(4), Tl(4A) and Tl(4B) sites inside the tunnel formed by the modulated $[(VO)_2(H_2O)_3SO_4)_3]^{2-}$ chains in the adjacent *A* layers (*b*). A schematic representation of the crystal structure of evdokimovite along the *c* axis (tunnels formed by the $[(VO)_2(H_2O)_3SO_4)_3]^{2-}$ chains = green ellipses, $[(VO)(H_2O)_2(SO_4)_2]^{2-}$ chains = green ticks) is shown in (*c*).

Tl4B sites). Analysis of the data listed in Table 8 shows that stereochemical activity of the so-called 'lone electron pairs' on the Tl^+ cations occurs in the structures with the presence of even moderate Lewis bases such as O atoms of terminal vanadyl ions and terminal O atoms of SO₄ groups, i.e. in karpovite and markhininite. The stereochemical behaviour of the lone electron pairs also favours lower coordination numbers and, as a consequence, smaller volumes of coordination poly-

hedra compared to structures with symmetrical coordination of Tl^+ cations (markhininite).

The remarkable presence of two different heteropolyhedral chains in the structure of evdokimovite points to its high complexity. In order to describe this in quantitative terms, we have applied the complexity approach developed recently by Krivovichev (2012, 2013, 2014). In the framework of this method, complexity is estimated as the amount of structural information



FIG. 7. Graphs of the [(VO)(H₂O)(SO₄)₂]²⁻, [(VO)(H₂O)₂(SO₄)₂]²⁻ and [(VO)₂(H₂O)₃SO₄)₃]²⁻ chains in the crystal structures of karpovite and evdokimovite (right) can be considered as derivatives from the graph of the [Bi(SO₄)₂]⁻ layers in markhininite (left) by the substitution of Bi³⁺ by V⁴⁺ and additional hydration.

contained in the unit cell of the crystal structure. More precisely, the amount of structural information per atom, I_G , is calculated as

$$I_G = -\sum_{i=1}^k p_i \log_2 p_i \text{ (bits/atom)}$$
(1),

whereas structural information per unit cell (u.c.), $I_{G,total}$, is calculated as

$$I_{G,total} = -v I_G = -v \sum_{i=1}^{k} p_i \log_2 p_i \text{ bits per unit cell (bits/u.c.)}$$
(2)

where k is the number of different crystallographic orbits (i.e. point systems occupied by symmetrically inequivalent atoms) and p_i is the random choice probability for an atom from the *i*th crystallographic orbit. This is

$$p_i = m_i / v \tag{3}$$

where m_i is a multiplicity of a crystallographic orbit relative to the reduced unit cell and v is the number of atoms in the reduced unit cell. Table 9 contains crystallographic data and complexity parameters for the natural and synthetic V4+ sulfates known to date. In order to account for the H atoms in the structures of karpovite and evdokimovite (that could be determined experimentally), their number and conditional Wyckoff positions have been added to the calculations and the disordered Tl sites in evdokimovite have been considered as a single site. It can be seen that the structures of both VOSO₄ polymorphs should be regarded as 'simple' structures (20-100 bits/u.c.; Krivovichev, 2013, 2014), whereas karpovite and other natural V⁴⁺ sulfates (bobjonesite, minasragrite, orthominasragrite and anorthominasragrite) have crystal structures of 'intermediate complexity' (100-500 bits/ u.c.). Among the synthetic compounds, most are intermediate in structural complexity, except for $Na_4(VO)(SO_4)_3$ and $K_4(VO)_3(SO_4)_5$ which are 'complex' (with amounts of structural information per unit cell between 500 and 1000 bits). It can be seen that evdokimovite has an $I_{G,total}$ value of ~1130 bits/u.c. and should therefore be identified as being 'very complex'. Its complexity can be compared to that of vesuvianite-group minerals which have structural information amounts per unit cell in the range 1050-1350 bits. It is remarkable that evdokimovite has the most complex structure among the compounds listed in Table 9. There is little doubt that the reason for this is that the crystal structure of evdokimovite contains vanadyl sulfate hydrate chains of two different topological types.

Considering the chemical compositions of the three minerals reported in this series of papers (markhininite, karpovite and evdokimovite), it is worth noting that karpovite and evdokimovite are hydrous species, atypical for fumarolic environments. Taking into account that these minerals are associated with bobjonesite, another vanadium sulfate hydrate, it may be suggested that karpovite, evdokimovite and bobjonesite formed as a result of the interaction of some primary anhydrous minerals with atmospheric water, a process frequently observed under laboratory conditions with minerals of fumarolic origin (e.g. formation of belloite, Cu(OH)Cl, as the result of reaction of melanothallite, Cu₂OCl₂, in moist air (Krivovichev et al., 2002).

Chemical formula	Mineral name	Space group	a (Å) / α (°)	b (Å) / β, (°)	c (Å) / γ, (°)	I_G (bits/atom)	$I_{G,total}$ bits/u.c.)	Refs.
α -VOSO ₄		P4/n	6.26 / 90		4.10 / 90	1.664	23.303	1
B-VOSO4	Pauflerite	Pnma	7.39 / 90	6.27 / 90	7.08 / 90	2.522	70.606	2
$VO(SO_4)(H_2O)_3$	Bobjonesite	$P2_1/n$	7.39 / 90	7.41 / 106.6	12.06 / 90	4.000	256.000	ю
$VO(SO_4)(H_2O)_5$	Minasragrite	$P2_{1/c}$	6.98 / 90	9.72 / 110.9	12.90 / 90	4.459	392.430	4
$VO(SO_4)(H_2O)_5$	Anorthominasragrite	$P\overline{1}$	7.53 / 79.0	7.79 / 71.9	7.82 / 65.4	4.248	161.421	5
$VO(SO_4)(H_2O)_5$	Orthominasragrite	$Pmn2_1$	7.24 / 90	9.32 / 90	6.19 / 90	3.823	168.215	9
$VO(SO_4)(H_2O)_5$)	$P\overline{1}$	7.47 / 101.9	10.14 / 95.5	6.20 / 92.1	4.644	232.193	7
$Na_4(VO)(SO_4)_3$		$P2_{1/c}$	8.65 / 90	16.00 / 90.0	15.51 / 90	5.392	905.909	8
$Na_2(VO)(SO_4)_2$		$P2_{1}2_{1}2_{1}$	6.30 / 90	6.80 / 90	16.68 / 90	3.807	213.212	6
K4(VO)3(SO4)5		$P2_1/n$	8.75 / 90	16.14 / 106.8	14.42 / 90	5.129	718.100	10
$H_2(VO)_2(SO_4)_3$		$P4_2/mnm$	8.97 / 90		15.59 / 90	3.195	242.842	11
$TI_{2}VO(SO_{4})_{2}(H_{2}O)$	Karpovite	$P2_1$	4.65 / 90	11.08 / 98.4	9.39 / 90	4.087	138.974	12
Tl4(VO)3(SO4)5(H2O)5	Evdokimovite	$P2_1/n$	6.30 / 90	10.11 / 90.3	39.43 / 90	5.644	1128.800	13
References: (1) Longo an	d Arnott (1970); (2) Krivov	richev <i>et al.</i> (2007);	; (3) Schindler et (al. (2003); (4) Tac	chez et al. (1979);	(5) Cooper <i>et al.</i>	(2003); (6) Hawt	horne <i>et</i>
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