

## KAINOTROPITE, $\text{Cu}_4\text{Fe}^{3+}\text{O}_2(\text{V}_2\text{O}_7)(\text{VO}_4)$ , A NEW MINERAL WITH A COMPLEX VANADATE ANION FROM FUMAROLIC EXHALATIONS OF THE TOLBACHIK VOLCANO, KAMCHATKA, RUSSIA

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### ABSTRACT

The new mineral kainotropite  $\text{Cu}_4\text{Fe}^{3+}\text{O}_2(\text{V}_2\text{O}_7)(\text{VO}_4)$  was found in sublimates of fumaroles related to the Tolbachik volcano, Kamchatka, Russia. The holotype specimen originates from the Yadovitaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption; associated minerals are hematite, langbeinite, calciolangbeinite, tenorite, piypite, lyonsite, rutile, pseudobrookite, sanidine, and lammerite. In paleo-fumarolic deposits of Mountain 1004 kainotropite is associated with diopside and hematite. It forms prismatic crystals up to  $0.2 \times 0.2 \times 0.5 \text{ mm}^3$ , isolated or combined in clusters up to 0.7 mm across. Kainotropite is iron-black to reddish-black, with semi-metallic luster.  $D_{\text{calc}}$  is  $4.10 \text{ g/cm}^3$ . In reflected light, kainotropite is grey, weakly anisotropic. The reflectance values [ $R_{\text{max}}-R_{\text{min}}$ , % ( $\lambda$ , nm)] are: 18.3–17.3 (470), 17.3–16.3 (546), 16.9–15.7 (589), 16.3–15.1 (650). The chemical composition of the holotype sample (wt.%, electron microprobe) is: CuO 46.69,  $\text{Al}_2\text{O}_3$  1.40,  $\text{Fe}_2\text{O}_3$  10.04,  $\text{TiO}_2$  0.32,  $\text{V}_2\text{O}_5$  37.58,  $\text{As}_2\text{O}_5$  2.55,  $\text{MoO}_3$  0.76, total 99.34. The empirical formula, based on 13 O *apfu*, is:  $\text{Cu}_{3.96}\text{Fe}_{0.85}\text{Al}_{0.19}\text{Ti}_{0.03}(\text{V}_{2.78}\text{As}_{0.15}\text{Mo}_{0.04})_{\Sigma 2.97}\text{O}_{13}$ . Kainotropite is orthorhombic, *Pnma*,  $a = 14.139(2)$ ,  $b = 6.7102(7)$ ,  $c = 11.4177(15)$  Å,  $V = 1083.3(2)$  Å<sup>3</sup>, and  $Z = 4$ . The strongest reflections of the powder XRD pattern [ $d$ , Å( $I$ )( $hkl$ )] are: 8.89(100)(101), 5.728(33)(002), 3.698(35)(212), 3.357(52)(020,203), 3.034(77)(220), 2.968(60)(303), and 2.655(27)(321,204). The crystal structure was solved from single-crystal XRD data,  $R = 0.085$ . Kainotropite represents a novel structure type.  $\text{Cu}^{2+}$  polyhedra (distorted tetragonal pyramids and strongly distorted octahedra) and  $\text{Fe}^{3+}$  octahedra are connected *via* common edges to form zigzag ribbons. Adjacent ribbons are connected by both  $\text{V}_2\text{O}_7$  and  $\text{VO}_4$  groups (isolated from each other) to form a heteropolyhedral pseudo-framework. The name kainotropite is derived from the Greek word *καινότροπος*, *unusual*, in allusion to its uncommon (for natural vanadates) anionic composition: it is the first mineral containing both pyrovanadate ( $\text{V}_2\text{O}_7$ )<sup>4-</sup> and orthovanadate ( $\text{VO}_4$ )<sup>3-</sup> anions.

**Keywords:** kainotropite, new mineral, copper iron vanadate, pyrovanadate, crystal structure, fumarole, Tolbachik volcano, Kamchatka.

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## INTRODUCTION

Vanadate mineralization of fumarolic origin is known at three active volcanoes, Izalco in El Salvador and Tolbachik and Bezmyannyi, both in Kamchatka, Russia. Despite being present in minor amounts overall, these minerals demonstrate significant species and structural diversity. All known fumarolic vanadates are hydrogen-free. Izalco is the type locality for seven copper vanadates, stoiberite  $\text{Cu}_5\text{O}_2(\text{VO}_4)_2$  (Birmie & Hughes 1979), ziesite  $\beta\text{-Cu}_2\text{V}_2\text{O}_7$  (orthorhombic) (Hughes & Birmie 1980), fingerite  $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$  (Hughes & Hadidiacos 1985), blossite  $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$  (monoclinic) (Robinson *et al.* 1987), lyonsite  $\text{Cu}_{3+2x}(\text{Fe}^{3+}_{4-2x}\text{Cu}_{2x})(\text{VO}_4)_6$ , with  $0 \leq x \leq 1$  (Hughes *et al.* 1987a), mcbirneyite  $\text{Cu}_3(\text{VO}_4)_2$  (Hughes *et al.* 1987b), and howardevansite  $\text{NaCu}^{2+}\text{Fe}^{3+}_2(\text{VO}_4)_3$  (Hughes *et al.* 1988). At Bezmyannyi, this chemical class of minerals is represented by two endemic species, koksharovite  $\text{CaMg}_2\text{Fe}^{3+}_4(\text{VO}_4)_6$  (Pekov *et al.* 2014) and ziminaite  $\text{Fe}^{3+}(\text{VO}_4)$  (Pekov *et al.* 2018a). The greatest number of fumarolic vanadates is known from Tolbachik. The majority of them contain species-defining  $\text{Cu}^{2+}$ : there are lyonsite (Pekov *et al.* 2013b), ziesite, blossite, fingerite, mcbirneyite (Pekov *et al.* 2018b), and 10 minerals endemic for Tolbachik, namely leningradite  $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$  (Vergasova *et al.* 1990), averievite  $\text{Cu}_6\text{O}_2(\text{VO}_4)_2\text{Cl}_2 \cdot n(\text{K,Cs,Rb})\text{Cl}$  (Vergasova *et al.* 1998), pseudolyonsite  $\text{Cu}_3(\text{VO}_4)_2$  (Zelenski *et al.* 2011), yaroshevskite  $\text{Cu}_9\text{O}_2(\text{VO}_4)_4\text{Cl}_2$  (Pekov *et al.* 2013c), starovaita  $\text{KCu}_5\text{O}(\text{VO}_4)_3$  (Pekov *et al.* 2013a), grigorievite  $\text{Cu}_3\text{Fe}^{3+}_2\text{Al}_2(\text{VO}_4)_6$  (Pekov *et al.* 2014), dokuchaevite  $\text{Cu}_8\text{O}_2(\text{VO}_4)_3\text{Cl}_3$  (Siidra *et al.* 2019a), aleutite  $\text{Cu}_5\text{O}_2(\text{AsO}_4)(\text{VO}_4) \cdot (\text{Cu}_{0.5}\square_{0.5})\text{Cl}$  (Siidra *et al.* 2019b), borisenkoite  $\text{Cu}_3[(\text{V,As})\text{O}_4]_2$  (Pekov *et al.* accepted), and as described in this paper, kainotropite  $\text{Cu}_4\text{Fe}^{3+}_2\text{O}_2(\text{V}_2\text{O}_7)(\text{VO}_4)$ . All these copper vanadates, except blossite and grigorievite, occur in the famous Yadovitaya fumarole.

The name kainotropite is derived from the Greek word  $\kappa\alpha\iota\acute{\nu}\tau\rho\pi\omicron\varsigma$ , *unusual*, in allusion to its previously unknown for natural vanadates anionic composition: it is the first mineral containing both pyrovanadate,  $(\text{V}_2\text{O}_7)^{4-}$ , and orthovanadate,  $(\text{VO}_4)^{3-}$ , anions. Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC), IMA No. 2015–053. The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with catalogue number 95603.

## OCCURRENCE AND GENERAL APPEARANCE

Kainotropite is one of the rarest minerals in the Tolbachik fumaroles. It was discovered in a single

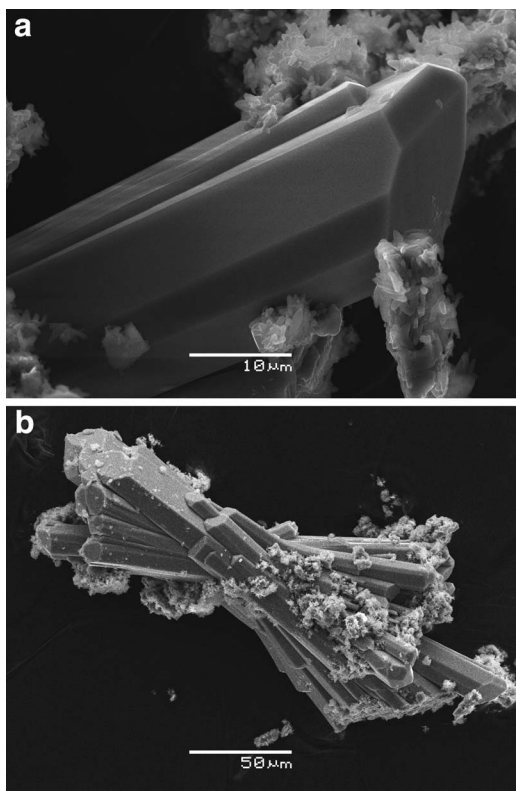


FIG. 1. Typical crystal (a) and aggregate composed of slightly divergent crystals (b) of kainotropite from the Yadovitaya fumarole. SEM (SE) images.

(holotype) specimen collected by us in July 2013 from the Yadovitaya fumarole situated at the summit of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption (NB GTFE), Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia ( $55^{\circ}41'N$   $160^{\circ}14'E$ , 1200 m asl).

The Second scoria cone of the NB GTFE is a monogenetic volcano about 300 m high and  $0.1 \text{ km}^3$  in volume formed in 1975 (Fedotov & Markhinin 1983) and demonstrating strong fumarolic activity to the present day. Yadovitaya is among the longest-living fumaroles at this scoria cone. It appeared immediately after GTFE (Vergasova & Filatov 2016) and remains active. The temperature measured by us using a chromel-alumel thermocouple in 2013 in the area where kainotropite was found varied in different pockets from 250 to 300 °C. We believe that kainotropite was deposited directly from hot gases as a volcanic sublimate at temperatures not lower than 300 °C.

TABLE 1. CHEMICAL COMPOSITION OF KAINOTROPITE

Constituent	1	2	3
CuO (wt.%)	46.69 (45.82–47.47)	46.59	47.43
ZnO	-	0.28	
Al <sub>2</sub> O <sub>3</sub>	1.40 (1.14–1.64)	0.75	
Fe <sub>2</sub> O <sub>3</sub>	10.04 (9.51–10.39)	11.12	11.90
TiO <sub>2</sub>	0.32 (0.07–0.51)	-	
V <sub>2</sub> O <sub>5</sub>	37.58 (36.40–40.45)	41.08	40.67
As <sub>2</sub> O <sub>5</sub>	2.55 (0.24–3.38)	-	
MoO <sub>3</sub>	0.76 (0.30–1.18)	-	
Total	99.34	99.82	
Formula calculated on the basis of 13 O <i>apfu</i>			
Cu	3.96	3.91	4
Zn	-	0.02	
Al	0.19	0.10	
Fe <sup>3+</sup>	0.85	0.93	1
Ti	0.03	-	
V	2.78	3.01	3
As	0.15	-	
Mo	0.04	-	

1 – Yadovitaya fumarole (holotype: average for 5 analyses, ranges are in parentheses), 2 – Mountain 1004, 3 – calculated for the idealized endmember formula Cu<sub>4</sub>Fe<sup>3+</sup>O<sub>2</sub>(V<sub>2</sub>O<sub>7</sub>)(VO<sub>4</sub>). Dash means that the content of a constituent is below the detection limit.

In the holotype specimen, kainotropite forms well-shaped prismatic crystals (up to 0.04 × 0.05 × 0.2 mm<sup>3</sup>) which are slightly divergent and combined in clusters (bunches) up to 0.1 × 0.25 mm (Fig. 1). They occur on langbeinite crust overgrowing basalt scoria. Kainotropite is intimately associated with hematite, tenorite, piypite, and an insufficiently characterized K-Na-Pb chlorosulfate. Other associated minerals are lyonsite, rutile (Fe- and Sb-enriched variety), pseudobrookite, sanidine (As-bearing variety), calciolangbeinite, and lammerite.

Recently, after completion of the investigation of the holotype and after the approval of kainotropite as a new species by the IMA CNMNC, this mineral was detected by us in a specimen collected in July 2018 from paleo-fumarolic deposits of Mountain 1004, a monogenetic volcano located 2 km south of the Second scoria cone of the NB GTFE. Mountain 1004 is a scoria cone formed as a result of an ancient eruption of Tolbachik. Fedotov & Markhinin (1983) evaluated its age as *ca.* 2000 years. Fumaroles located at Mountain 1004 are completely extinct, however, many sublimate minerals, except of water-soluble species, have been preserved. Kainotropite was found at the Southern fumarole field. The mineral occurs

here as prismatic crystals up to 0.2 × 0.2 × 0.5 mm<sup>3</sup>, isolated or combined in clusters up to 0.7 mm across. The crystals overgrow volcanic scoria strongly altered by fumarolic gas. Kainotropite is associated here with diopside and hematite; supergene minerals observed in this specimen are volborthite, brochantite, gypsum, and opal.

#### PHYSICAL PROPERTIES AND OPTICAL DATA

Kainotropite is iron-black to reddish-black with strong semi-metallic luster. It is opaque in crystals but translucent, dark red in very thin sections (like hematite). The streak is dark brown-red. The mineral is brittle; cleavage or parting is not observed. The fracture is uneven (observed under the scanning electron microscope). The mean micro-indentation hardness (VHN) is 481, range is 432–531 kg/mm<sup>2</sup> (load 20 g). Mohs' hardness was not measured directly due to the small size of the crystals; the value calculated from the micro-indentation hardness is *ca.* 5. Density could not be measured because of the scarcity of material. Density calculated using the empirical formula of the holotype is 4.104 g/cm<sup>3</sup>.

Under the microscope in reflected light, the mineral is grey; pleochroism was not observed. Bireflectance is weak,  $\Delta R = 1.2\%$  (589 nm). Anisotropism is weak. Strong brown-red internal reflections were observed. The reflectance values measured in air by means of a MSF-21 microspectrophotometer (LOMO, Russia) using the SiC standard (Zeiss, No. 545) are reported in Table S1 (Supplementary data)<sup>1</sup>.

#### CHEMICAL COMPOSITION

The chemical composition of kainotropite was determined in the Laboratory of Analytical Techniques of High Spatial Resolution, Department of Petrology, Moscow State University, using a JEOL JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer, with an accelerating voltage of 20 kV, a beam current of 20 nA, and a 3 μm beam diameter. The standards used were: CuFeS<sub>2</sub> (Cu and Fe), ZnS (Zn), Al<sub>2</sub>O<sub>3</sub> (Al), ilmenite (Ti), V (V), FeAsS (As), and CaMoO<sub>4</sub> (Mo). Contents of other elements with atomic numbers higher than oxygen are below their detection limits.

<sup>1</sup> Supplementary Data are available from the Depository of Unpublished data on the MAC website (<http://mineralogicalassociation.ca/>), document "Kainotropite, CM58, 19-00073".

TABLE 2. POWDER X-RAY DIFFRACTION DATA ( $d$  IN Å) FOR KAINOTROPITE

$l_{\text{obs}}$	$d_{\text{obs}}$	$l_{\text{calc}}^*$	$d_{\text{calc}}^{**}$	$hkl$
<b>100</b>	<b>8.89</b>	100	8.883	101
<b>33</b>	<b>5.728</b>	16	5.709	002
18	5.363	11	5.354	111
12	4.441	10	4.441	202
9	4.379	8	4.356	301
8	4.156	2	4.156	112
<b>35</b>	<b>3.698</b>	26	3.704	212
25	3.651	28	3.654	311
12	3.533	15	3.535	400
<b>52</b>	<b>3.357</b>	29, 14	3.355, 3.351	020, 203
12	3.311	2	3.310	013
7	3.233	5	3.223	113
<b>77</b>	<b>3.034</b>	63	3.031	220
14	2.992	5	3.005	402
<b>60</b>	<b>2.968</b>	95	2.961	303
21	2.756	12, 4	2.745, 2.743	501, 412
<b>27</b>	<b>2.655</b>	6, 7	2.658, 2.647	321, 204
23	2.479	25	2.478	123
21	2.435	26	2.433	420
17	2.279	6, 11	2.294, 2.270	314, 503
18	2.223	25, 2	2.221, 2.220	404, 323
7	2.170	3	2.174	024
5	2.136	1, 5	2.137, 2.133	115, 230
4	2.073	4	2.078	224
8	1.991	6, 6	1.998, 1.990	232, 331
3	1.917	1	1.918	405
6	1.883	11	1.880	523
4	1.816	2	1.816	116
6	1.768	2, 9	1.772, 1.767	216, 800
4	1.755	15	1.754	614
9	1.709	6, 1, 9	1.711, 1.709, 1.708	721, 810, 234
8	1.681	25	1.678	040
10	1.601	7, 15	1.601, 1.598	714, 624
12	1.575	16, 1	1.575, 1.575	723, 117
4	1.519	3, 1	1.516, 1.516	911, 440
7	1.467	5	1.466	814
10	1.456	18, 2	1.460, 1.459	343, 127
8	1.411	3, 10	1.412, 1.410	921, 634
5	1.368	3	1.367	640
4	1.340	7	1.339	444
5	1.330	4	1.327	734
6	1.320	4	1.318	037
12	1.306	6, 10	1.308, 1.303	128, 10.2.0
6	1.235	6	1.235	437

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

Chemical data for kainotropite are given in Table 1. The empirical formula of the holotype sample calculated on the basis of 13 O atoms per formula unit (*apfu*) is  $\text{Cu}_{3.96}\text{Fe}^{3+}_{0.85}\text{Al}_{0.19}\text{Ti}_{0.03}(\text{V}_{2.78}\text{As}_{0.15}\text{Mo}_{0.04})_{\Sigma 2.97}\text{O}_{13}$ . The idealized formula is  $\text{Cu}_4\text{Fe}^{3+}\text{O}_2(\text{V}_2\text{O}_7)(\text{VO}_4)$ .

#### X-RAY CRYSTALLOGRAPHY

Powder X-ray diffraction (XRD) data for kainotropite (Table 2) were collected for the holotype sample with a Rigaku R-AXIS Rapid II diffractometer equipped with a cylindrical image plate detector

TABLE 3. CRYSTAL DATA, DATA COLLECTION INFORMATION, AND STRUCTURE REFINEMENT DETAILS FOR KAINOTROPITE

Formula	$\text{Cu}_4(\text{Fe}_{0.88}\text{Al}_{0.12})\text{O}_2(\text{V}_2\text{O}_7)(\text{VO}_4)$
Formula weight	667.37
Temperature, K	293(2)
Radiation and wavelength, Å	MoK $\alpha$ ; 0.71073
Crystal system, space group; Z	Orthorhombic, <i>Pnma</i> ; 4
Unit-cell dimensions, Å	$a = 14.139(2)$ $b = 6.7102(7)$ $c = 11.4177(15)$
$V$ , Å <sup>3</sup>	1083.3(2)
Absorption coefficient $\mu$ , mm <sup>-1</sup>	11.388
$F_{000}$	1254
Crystal size, mm <sup>3</sup>	$0.01 \times 0.02 \times 0.03$
Diffractometer	Xcalibur S CCD
$\theta$ range for data collection, °	2.88–28.28
Index ranges	$-18 \leq h \leq 18$ , $-8 \leq k \leq 8$ , $-15 \leq l \leq 15$
Reflections collected	15728
Independent reflections	1450 ( $R_{\text{int}} = 0.2951$ )
Independent reflections with $I > 2\sigma(I)$	719
Data reduction	CrysAlisPro, version 1.171.37.34 (Agilent Technologies 2014)
Absorption correction	multi-scan [empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm]
Structure solution	direct methods
Refinement method	full-matrix least-squares on $F^2$
Number of refined parameters	116
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0854$ , $wR2 = 0.1625$
$R$ indices (all data)	$R1 = 0.1781$ , $wR2 = 0.2031$
GoF	1.025
Largest diff. peak and hole, e/Å <sup>3</sup>	3.85 and $-1.49$

(radius 127.4 mm) using Debye-Scherrer geometry, CoK $\alpha$  radiation (rotating anode with VariMAX micro-focus optics), 40 kV, 15 mA, and an exposure time of 10 min. The angular resolution of the detector is 0.045 2 $\theta$  (pixel size 0.1 mm). The data were integrated using the software package Osc2Tab (Britvin *et al.* 2017). The parameters of the orthorhombic unit cell calculated from the powder data are  $a = 14.165(4)$ ,  $b = 6.713(2)$ ,  $c = 11.414(3)$  Å, and  $V = 1085(1)$  Å<sup>3</sup>.

Single-crystal XRD studies of kainotropite from both the Yadovitaya fumarole (holotype) and Mountain 1004 were carried out using a four-circle Xcalibur S diffractometer equipped with a CCD detector. A complete sphere of three-dimensional data was collected from a single crystal selected from the holotype specimen. Intensity data were corrected for Lorentz and polarization effects. The crystal structure of kainotropite was solved by direct methods and refined on the basis of 719 independent reflections with  $I > 2\sigma(I)$  to  $R_1 = 0.085$  using the SHELX software package (Sheldrick 2008). The relatively high value of  $R_1$  is assumed to be caused by small crystal

size and the non-perfect quality of the studied crystal. Crystal data, data collection information, and structure refinement details are reported in Table 3; atom coordinates, displacement parameters, and bond-valence calculations are given in Tables 4, S2, and S3 (Supplementary data); and selected interatomic distances are reported in Table 5.

The parameters of the orthorhombic unit cell obtained for a single crystal from Mountain 1004 are  $a = 14.187(7)$ ,  $b = 6.735(2)$ ,  $c = 11.423(7)$  Å and  $V = 1091.5(9)$  Å<sup>3</sup>.

## DISCUSSION

### *Crystal structure*

The crystal structure of kainotropite (Fig. 2) is unique. Its most unusual feature is the presence of a complex vanadate anion consisting of pyrovanadate groups, V<sub>2</sub>O<sub>7</sub>, and single VO<sub>4</sub> tetrahedra isolated from each other. V<sup>5+</sup> occupies three crystallographically non-equivalent sites (Table 4). V(1)- and V(2)-centered tetrahedra are connected *via* the O(1) vertex

TABLE 4. ATOM COORDINATES, EQUIVALENT DISPLACEMENT PARAMETERS ( $U_{\text{eq}}$ , IN  $\text{\AA}^2$ ), SITE MULTIPLICITIES (Q), AND BOND-VALENCE SUMS (BVS) FOR KAINOTROPITE

Site	x	y	z	$U_{\text{eq}}$	Q	BVS*
Cu(1)	0.1430(2)	¼	-0.2459(2)	0.0182(7)	4	2.07
Cu(2)	0.00559(14)	0.5051(3)	0.14547(16)	0.0183(5)	8	2.12
Cu(3)	0.6397(2)	¼	0.2055(2)	0.0177(7)	4	1.94
Fe = Fe <sub>0.877(12)</sub> Al <sub>0.12</sub>	0.3580(2)	½	0.5202(3)	0.0150(11)	4	3.06
V(1)	0.1372(3)	½	0.6680(3)	0.0131(9)	4	4.87
V(2)	0.3624(3)	¼	-0.1176(3)	0.0139(9)	4	5.07
V(3)	0.1920(3)	½	0.0245(3)	0.0131(8)	4	5.26**
O(1)	0.0881(11)	½	0.5284(13)	0.021(4)	4	2.15
O(2)	0.0580(10)	¼	0.1608(11)	0.011(3)	4	2.21
O(3)	0.2558(11)	½	0.6455(13)	0.016(3)	4	1.96
O(4)	0.2419(13)	¼	0.4067(13)	0.026(4)	4	2.02
O(5)	0.7375(11)	¼	-0.1382(14)	0.015(3)	4	2.10
O(6)	0.8839(7)	0.4578(16)	-0.0261(8)	0.018(2)	8	2.02
O(7)	0.3981(7)	0.0357(15)	0.2396(8)	0.014(2)	8	1.98
O(8)	0.0524(10)	¼	-0.1178(11)	0.010(3)	4	2.04
O(9)	0.3953(7)	0.4553(16)	-0.1899(9)	0.013(2)	8	1.90
O(10)	0.2440(13)	¼	-0.0942(13)	0.024(4)	4	2.10

\* Parameters for bond-valence calculations are taken from Gagné & Hawthorne (2015); for full data see Table S3 (Supplementary data). \*\* Could be slightly decreased if admixed As is present at the V(3) site.

to form  $\text{V}_2\text{O}_7$  groups [in both tetrahedra the distance between  $\text{V}^{5+}$  and the bridging O(1) atom is the longest one: V(1)–O(1) is 1.738(16) Å and V(2)–O(1) is 1.808(14) Å] while V(3)-centered tetrahedra are isolated. The mean V–O distances are 1.72, 1.71, and 1.70 Å for V(1), V(2), and V(3)-centered tetrahedra, respectively. The  $\text{Cu}^{2+}$  cations occupy three crystallographically non-equivalent sites. Cu(1)

and Cu(3) cations center distorted tetragonal pyramids with four short Cu–O bonds [Cu–O distances lie in the ranges 1.880(17) to 2.010(10) Å for Cu(1) and 2.010(10) to 2.046(11) Å for Cu(3)] and one elongated Cu–O bond [2.244(17) Å for Cu(1) and 2.254(17) Å for Cu(3)]. Cu(2) cations occupy octahedra strongly distorted due to the Jahn-Teller effect: four short Cu(2)–O distances are in the range 1.864(7) to 2.089(10) Å and two elongated bonds have distances 2.360(10) and 2.627(10) Å. The  $\text{Fe}^{3+}$  cations (with admixed Al; the refined Fe:Al ratio is 0.88:0.12, Table 4) center octahedra with the cation-anion distances varying from 1.946(17) to 2.034(15) Å (Table 5). Copper- and Fe-centered polyhedra are connected with each other *via* common edges to form zigzag ribbons running along the **b** axis (Fig. 3a). Adjacent ribbons are connected *via* O atoms of V-centered tetrahedra, involving both  $\text{V}_2\text{O}_7$  and  $\text{VO}_4$  groups, to form (100) “layers” (Fig. 3b). These “layers” are also linked by  $\text{V}_2\text{O}_7$  groups and isolated  $\text{VO}_4$  tetrahedra, forming a dense, three-dimensional heteropolyhedral pseudo-framework (Fig. 2).

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF KAINOTROPITE

Cu(1)–O(5)	1.880(17)	Fe–O(10)	1.946(17)
–O(8)	1.944(13)	–O(6)	1.995(11) ×2
–O(7)	2.010(10) ×2	–O(2)	1.996(14)
–O(10)	2.244(17)	–O(8)	2.022(14)
		–O(3)	2.034(15)
Cu(2)–O(8)	1.864(7)		
–O(2)	1.874(6)	V(1)–O(3)	1.696(16)
–O(7)	2.026(10)	–O(7)	1.728(10) ×2
–O(6)	2.089(10)	–O(1)	1.738(16)
–O(9)	2.360(10)		
–O(6)	2.627(10)	V(2)–O(9)	1.672(10) ×2
Cu(3)–O(2)	1.915(14)	–O(10)	1.695(18)
–O(4)	1.931(17)	–O(1)	1.808(14)
–O(9)	2.046(11) ×2		
–O(3)	2.254(17)	V(3)–O(5)	1.637(17)
		–O(4)	1.637(16)
		–O(6)	1.760(11) ×2

#### Comparative crystal chemistry

No vanadates or other compounds closely related to kainotropite are known, but some crystal chemical resemblance is observed between kainotropite and epidote-group silicates having the same general stoichiometry,  $\text{Me}_5\text{X}_2(\text{Si}_2\text{O}_7)(\text{SiO}_4) = \text{Me}_1\text{Me}_2\text{Me}_3\text{X}_2$

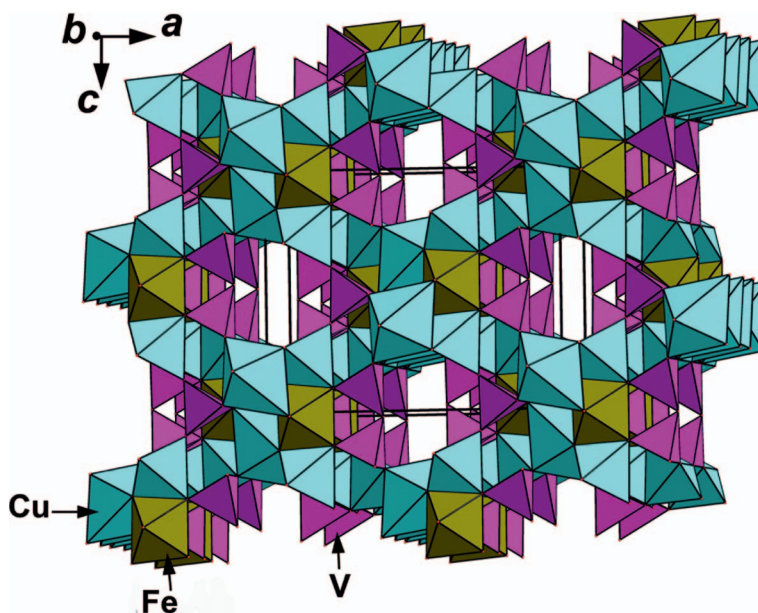


FIG. 2. The crystal structure of kainotropite. The unit cell is outlined.

( $\text{Si}_2\text{O}_7$ )( $\text{SiO}_4$ ), with species-defining  $Me1 = \text{Ca}, \text{Mn}^{2+}, \text{Sr}, \text{Pb}^{2+}, \text{REE}^{3+}$ ;  $Me2 = \text{Al}, \text{Fe}^{3+}, \text{Fe}^{2+}, \text{Mn}^{3+}, \text{Mn}^{2+}, \text{Mg}, \text{V}^{3+}$ ;  $X = \text{O}, \text{OH}, \text{F}$  (Armbruster *et al.* 2006). The only orthorhombic epidote-group member, zoisite  $\text{Ca}_2\text{Al}_3\text{O}(\text{OH})(\text{Si}_2\text{O}_7)(\text{SiO}_4)$  (Dollase 1968, Dörsam *et al.* 2007), is similar to kainotropite in some aspects: both minerals are characterized by the same space

group,  $Pnma$ , and comparable unit-cell dimensions (Table 6) and by similar arrangements of pyrogroups and isolated tetrahedra (Fig. 4). At the same time, their powder XRD patterns and physical properties are different (Table 6) because of the essential chemical difference.

TABLE 6. COMPARATIVE DATA FOR KAINOTROPITE AND ZOISITE

Mineral	Kainotropite	Zoisite
Formula	$\text{Cu}_4\text{Fe}^{3+}\text{O}_2(\text{V}_2\text{O}_7)(\text{VO}_4)$	$\text{Ca}_2\text{Al}_3\text{O}(\text{OH})(\text{Si}_2\text{O}_7)(\text{SiO}_4)$
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pnma$	$Pnma$
$a, \text{Å}$	14.139(2)	16.19–16.28
$b, \text{Å}$	6.7102(7)	5.55–5.57
$c, \text{Å}$	11.4177(15)	10.03–10.14
$V, \text{Å}^3$	1083.3(2)	901–919
$Z$	4	4
Strongest reflections of the X-ray powder pattern: $d (\text{Å}), l$	8.89, 100 5.728, 33 3.698, 35 3.357, 52 3.034, 77 2.968, 60 2.655, 27	8.09, 40 5.01, 30 4.03, 50 2.874, 65 2.693, 100 2.019, 35 1.601, 35
References	this work	Dollase (1968); Anthony <i>et al.</i> (1995); Dörsam <i>et al.</i> (2007)

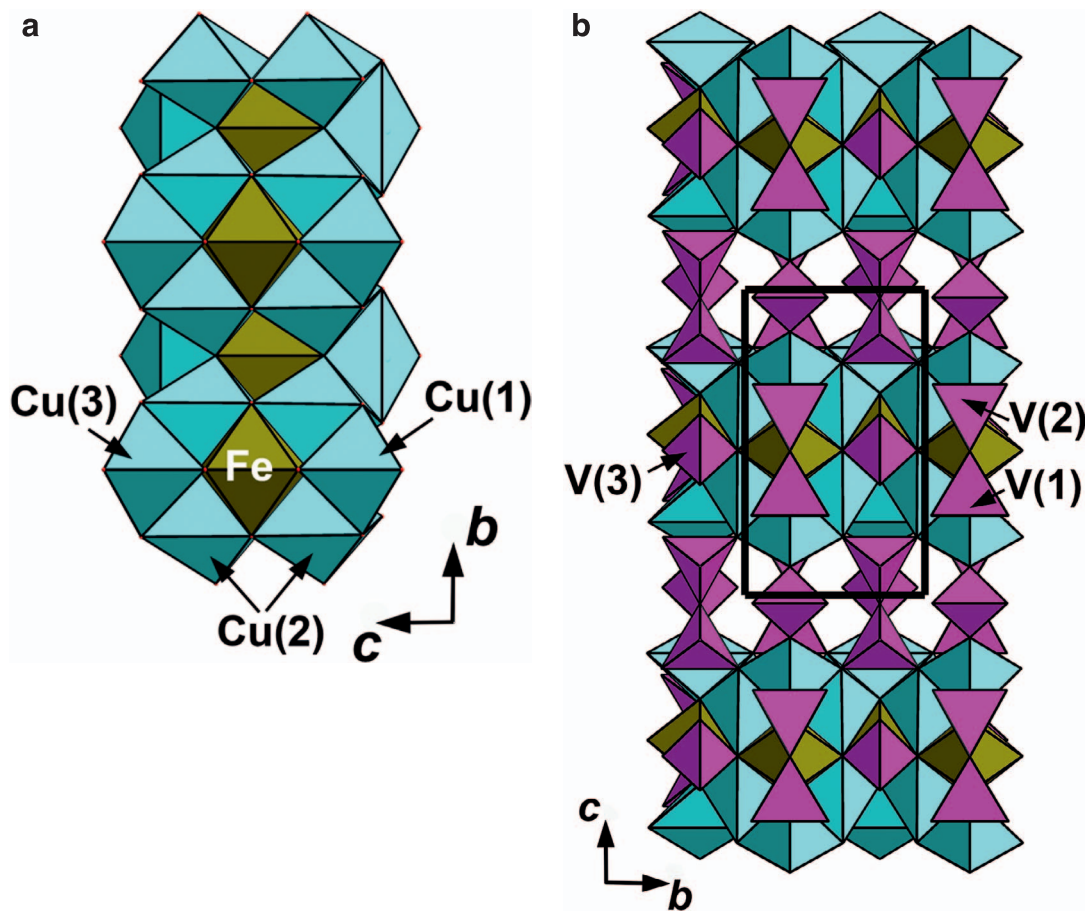


FIG. 3. The ribbons formed by Fe- and Cu-centered polyhedra (a) and heteropolyhedral “layers” made up of the ribbons connected *via*  $V_2O_7$  pyrovanadate groups and isolated  $VO_4$  tetrahedra in the structure of kainotropeite. The unit cell is outlined in (b).

Kainotropeite is the first mineral containing both pyrovanadate ( $V_2O_7$ ) and orthovanadate ( $VO_4$ ) tetrahedral groups. Among synthetic vanadates, such a combination is known, *e.g.*, in  $KBaCd_2(VO_4)(V_2O_7)$  (Münchau & Müller-Buschbaum 1996),  $RbCd_3(VO_4)(V_2O_7)$  (Mertens & Müller-Buschbaum 1997),  $Na_6Mg_2(VO_4)_2(V_2O_7)$  (Mitiaev *et al.* 2004),  $Pb_2V^{3+}O(VO_4)(V_2O_7)_{0.5}$  (Henry *et al.* 2002), and  $[La(UO_2)(V_2O_7)][(UO_2)(VO_4)]$  (Mer *et al.* 2012).

The structure of kainotropeite could also be described in terms of anion-centred tetrahedra (Krivovichev *et al.* 2013). Its formula in this aspect can be written as  $[O_2Cu_4Fe^{3+}][(V_2O_7)(VO_4)]$ . The  $OCu_3Fe$  tetrahedra are connected *via* common Cu(2) vertices forming pyroxene-like chains. Pairs of such chains are connected with each other *via* common Fe

vertices (Fig. 5a). Thus, in the structure of kainotropeite double chains (ribbons) of oxocentered tetrahedra  $[O_4Cu_8Fe^{3+}_2]$  parallel to the *b* axis are present (Fig. 5b). Pyroxene-like chains of  $OCu_4$  tetrahedra are known in kamchatkite  $K_2[O_2Cu_6][SO_4]_4Cl_2$  (Varaksina *et al.* 1990), chloromenite  $Cu_3[O_2Cu_6][SeO_3]_4Cl_6$  (Krivovichev *et al.* 1998), vergasovaite  $[O_2Cu_6][(Mo,S)O_4SO_4]_2$  (Berlepsch *et al.* 1999), cupromolybdate  $[O_2Cu_6][MoO_4]_4$  (Zelenski *et al.* 2012), yaroshevskite  $Cu_3[O_2Cu_6][VO_4]_4Cl_2$  (Pekov *et al.* 2013b), synthetic  $[OCu_3][V_2O_7](H_2O)$  (Leblanc & Ferey 1990), and some other compounds. Double chains of vertex-shared oxocentered tetrahedra have been described in ludwigite-group members and related borates with the general formula  $Me_1_2Me_2O_2(BO_3)$  in which  $Me_1 = Mg, Fe^{2+}, Mn^{2+}, Ni^{2+}$  and  $Me_2$



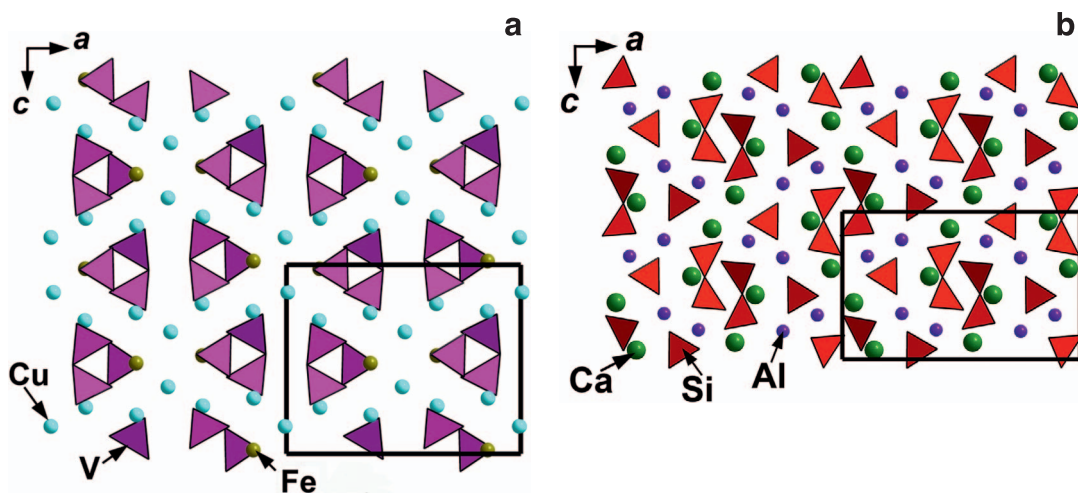


FIG. 4. Arrangement of tetrahedral pyrogroups and isolated tetrahedra in kainotropite (a) and zoisite (b; drawn after Dollase 1968). Di- and trivalent metal cations are shown as spheres. The unit cells are outlined.

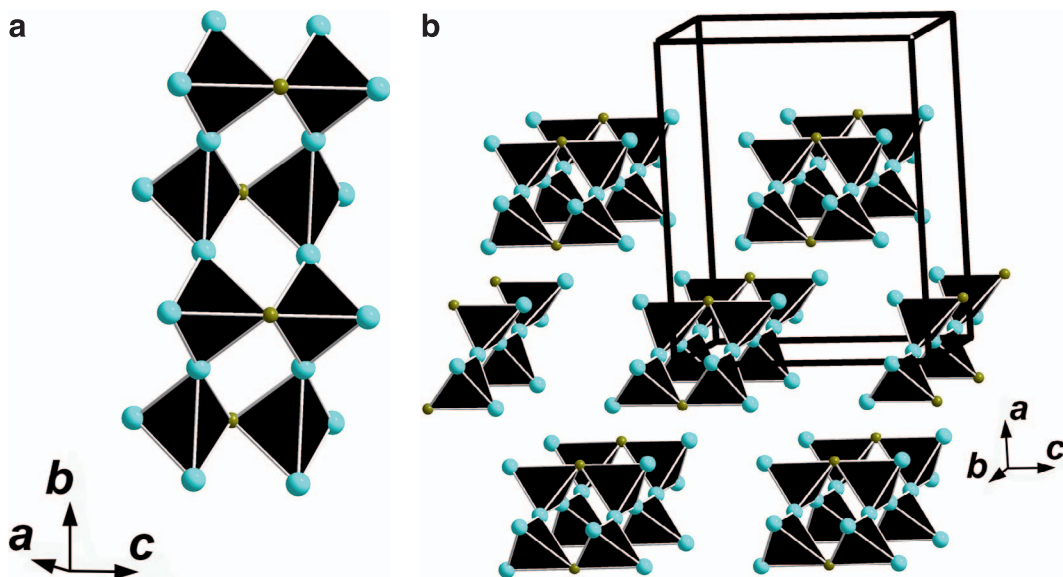


FIG. 5. Oxocentered tetrahedral double chain (a) and the arrangement of such chains in the structure of kainotropite. Copper atoms are shown as blue spheres and Fe atoms as olive green spheres. The unit cell is outlined in (b).

=  $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$ , Al,  $\text{Ti}^{4+}$ ,  $\text{Sb}^{5+}$ . These double chains [ $\text{O}_2\text{Me}_5$ ], which are classified as C2 (Krivovichev & Filatov 2001), are different in configuration from the double chains found in kainotropite. Thus, the motif of oxocentered tetrahedra in kainotropite is unique.

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