

Original paper

Karpenkoite, $\text{Co}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, a cobalt analogue of martyite from the Little Eva mine, Grand County, Utah, USA

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Karpenkoite (IMA 2014-092), ideally $\text{Co}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, is a new divanadate mineral species, the cobalt analogue of martyite, found at the Little Eva mine, Grand County, Utah, USA. It occurs on sandstone matrix in close association with martyite, quartz, gypsum, baryte, roscoelite and an unidentified Al vanadate. Karpenkoite is a secondary mineral formed during the post-mining oxidation of corvusite and montroseite in a moist environment at ambient temperatures. The new mineral occurs as lamellar crystals, coarsely hexagonal or irregular in shape, typically curved. The crystals form rose-like clusters or globular aggregates up to 0.2 mm across. Karpenkoite is orange with pale yellow-orange streak. It is transparent with a vitreous luster. The mineral is brittle, with laminated fracture and perfect cleavage on {001}. The calculated density is 3.415 g cm^{-3} . The mineral is optically uniaxial (+), with $\omega = 1.827(8)$ and $\varepsilon = 1.843(8)$. The chemical composition of karpenkoite (wt. %, electron-microprobe data) is: MgO 0.05, CaO 0.26, MnO 1.39, CoO 33.22, NiO 2.02, CuO 0.28, ZnO 12.66, V_2O_5 38.70, H_2O (calc.) 11.61, total 100.19. The empirical formula, calculated on the basis of 11 O *apfu*, is $(\text{Co}_{2.06}\text{Zn}_{0.72}\text{Ni}_{0.13}\text{Mn}_{0.09}\text{Ca}_{0.02}\text{Cu}_{0.02}\text{Mg}_{0.01})_{\Sigma 3.05}\text{V}_{1.98}\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. The Raman spectrum demonstrates symmetric stretching and bending vibrations of V^{5+}O_3 units and the O–H stretching and bending vibrations of the H_2O molecules. The new mineral is trigonal, the most probable space group is $P\bar{3}m1$ (by analogy with its Zn analogue martyite), $a = 6.016(4)$, $c = 7.234(6) \text{ \AA}$, $V = 226.7(2) \text{ \AA}^3$ and $Z = 1$. The strongest powder X-ray diffraction lines are [d_{obs} , $\text{Å}(J)(hkl)$]: 7.15(100)(001), 5.19(18)(010), 4.20(25)(101,011), 3.59(21)(002), 2.95(54)(012,102), 2.77(21)(111), 2.60(36)(200), and 2.44(33)(201,021). The new mineral is named in honor of the Russian mineralogist Vladimir Yu. Karpenko (b. 1965), an expert on the mineralogy of vanadium.

Keywords: karpenkoite, new mineral, cobalt divanadate, powder diffraction, Little Eva mine, Utah

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1. Introduction

Natural divanadates, *i.e.*, minerals with the $[\text{V}_2\text{O}_7]^{4-}$ group as the species-defining anion, are not numerous. To date, only seven such minerals are known. Among them, four species are H-bearing, namely volborthite, $\text{Cu}_3(\text{V}_2\text{O}_7)(\text{OH})_2(\text{H}_2\text{O})_2$ (Volborth and Hess 1838), fianelite, $\text{Mn}_2\text{V}(\text{V,As})\text{O}_7(\text{H}_2\text{O})_2$ (Brugger and Berlepsch 1996), martyite, $\text{Zn}_3(\text{V}_2\text{O}_7)(\text{OH})_2(\text{H}_2\text{O})_2$ (Kampf and Steele 2008), and engelhauptite, $\text{KCu}_3(\text{V}_2\text{O}_7)(\text{OH})_2\text{Cl}$ (Pekov et al. 2015), and three are anhydrous: chervetite, $\text{Pb}_2\text{V}_2\text{O}_7$ (Bariand et al. 1963), ziesite, $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ (Hughes and Birnie 1980), and blossite, $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ (Robinson et al. 1987). All of them, except volborthite, are very rare.

Here we present the mineralogical description of a new divanadate mineral karpenkoite (pronounced ‘kar pen

kou ait’; Cyrillic – карпенкоит), $\text{Co}_3(\text{V}_2\text{O}_7)(\text{OH})_2(\text{H}_2\text{O})_2$, the cobalt analogue of martyite, named in honor of the prominent Russian mineralogist Vladimir Yur’evich Karpenko (born 1965), who works as scientific researcher at the Fersman Mineralogical Museum of the Russian Academy of Sciences in Moscow. Vladimir Karpenko is especially known for his contribution to the mineralogy of vanadium (Karpenko 1993; Karpenko et al. 2004, 2005, 2009, 2011).

The new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2014-092). The holotype specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, under catalogue number 94997.

2. Occurrence

Specimens containing karpenkoite were collected underground by one of the authors (BT) at the Little Eva mine, Yellow Cat District, Grand County, Utah, USA (38°50'17"N, 109°31'35"W) in September 1999. This mine belongs to a group of deposits that were worked intensively for uranium and vanadium from the 1940's to the 1970's. The ore ranged in grade from a fraction of a percent to 10 % V_2O_5 and up to 0.4 % U_3O_8 (Stokes and Mobley 1954). Mineralization was developed in the Salt Wash member of the Jurassic Morrison Formation. The Salt Wash member forms the lower part of the Morrison Fm. and consists of about equal proportions of gray, lenticular, cross-bedded sandstone, and gray and red mudstone with a few limestone and chert beds. Stokes and Mobley (1954) particularly underlined that the conglomeratic sandstone is vanadium-bearing in several places.

The sandstone forms either a stratum composed of a single lenticular bed (from ~0.3 to ~6 m thick) or strata composed of many lenticular beds which may have a total thickness of more than ~24 m. Typically, the Salt Wash member includes a basal sandstone unit, one or more intermediate sandstone units, and a top sandstone unit. Strata between the sandstone units consist of dominantly greyish and reddish mudstones and claystones with minor sand lenses. Sandstone accounts for *c.* 58 % by volume, mudstone 41 % and limestone 1 %. The ore deposits in the Salt Wash member are generally tabular bodies that appear to be localized in the thicker parts of sandstone lenses. Within a mineralized layer, high-grade concentrations of uranium and vanadium minerals occur in bodies or pods commonly associated with carbonaceous material (Newman 1962).

Mining operations at the Little Eva mine, which were stopped in 1979, exposed primary and secondary vana-

dium mineralization. Karpenkoite and closely associated martyite were formed as a result of the supergene oxidation of the primary vanadium minerals corvusite and montroseite in a moist environment at ambient temperatures.

Karpenkoite is a very rare mineral. It was found on sandstone blocks in close association with its zinc analogue martyite, quartz, abundant gypsum, baryte, roscoelite, and an unidentified Al vanadate. Other supergene minerals identified at the site include andersonite, ansermetite, calciodelrioite (Kampf et al. 2012), calcite, carnotite, cobaltomenite, dickthomssenite, ferroselite, huemulite, hughesite, lasalite, melanovanadite, metarosite, nashite (Kampf et al. 2013), native selenium, natrozippite, nestolaite (Kasatkin et al. 2014), orschallite, pascoite, rossite, schröckingerite, sherwoodite, tyuyamunite and also secondary uraninite.

3. General appearance, physical properties and optical data

Karpenkoite forms orange lamellar crystals up to 0.05 mm across (usually much smaller), coarsely hexagonal or irregular in shape, typically curved. The crystals grow in groups, rose-like clusters or globular aggregates up to 0.2 mm across (Figs 1–2). These aggregates occur in interstices and small cavities between quartz grains in the mineralized sandstone (Fig. 3).

Karpenkoite is transparent, with a pale yellow-orange streak and vitreous luster. It is non-fluorescent under ultraviolet irradiation or when exposed to cathode rays. The mineral is brittle, with laminated fracture and perfect cleavage on {001}. The Mohs hardness could not be measured because of tiny size of crystals and openwork character of aggregates; it is probably about 3, by anal-

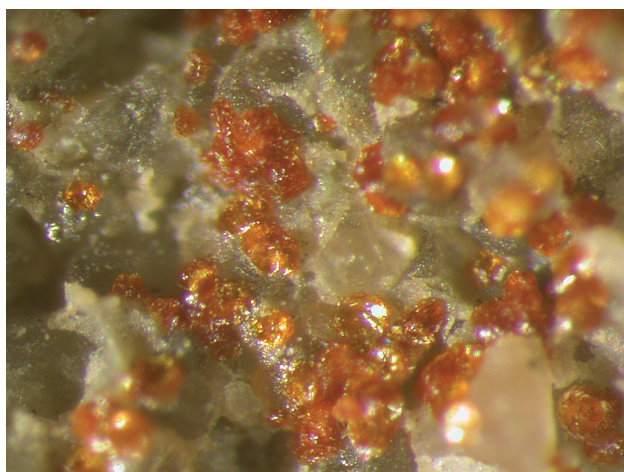


Fig. 1 Clusters and globular aggregates of orange karpenkoite crystals overgrowing sandstone. Image 1 mm wide.

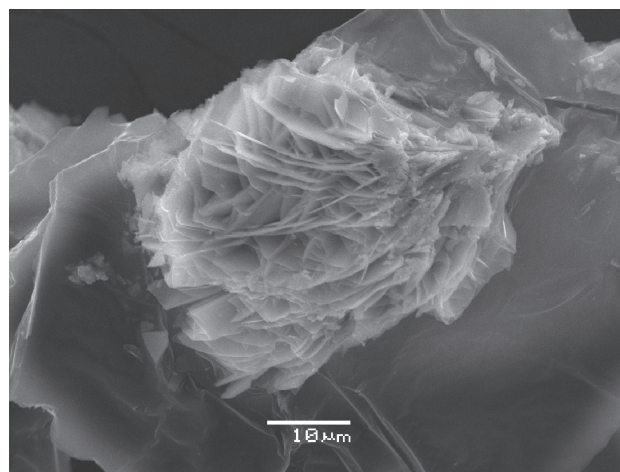


Fig. 2 A typical rose-like cluster of lamellar karpenkoite crystals; SEM (SE) image.

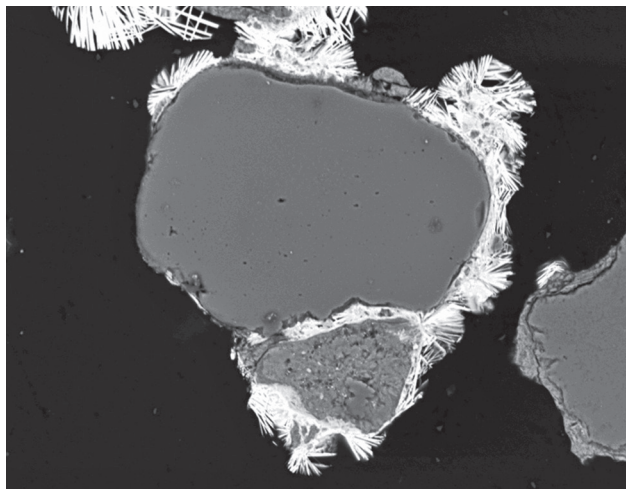


Fig. 3 Bunches and globular aggregates of divergent lamellar and acicular-looking crystals (white) of karpenkoite overgrowing the grains of quartz (gray) in the mineralized sandstone. A SEM (BSE) image 0.33 mm wide.

ogy with martyrite. Karpenkoite is insoluble in H_2O but easily soluble in cold diluted HCl or HNO_3 . Its density was not measured due to the paucity of pure material. The calculated density based on the empirical formula is 3.415 g cm^{-3} .

The new mineral is optically uniaxial (+), with $\omega = 1.827(8)$ and $\varepsilon = 1.843(8)$ (measured at 589 nm). In transmitted light, karpenkoite is reddish-brown and non-pleochroic.

The Gladstone-Dale compatibility index $1 - (K_p/K_c)$ is 0.053 that is rated as good (calculated for the empirical formula).

4. Chemical composition

The chemical composition of karpenkoite (Tab. 1) was determined using a JEOL Superprobe 733 scanning electron microscope (SEM) equipped with an INCA energy-dispersive X-ray spectrometer. An operating voltage of 20 kV was used with a beam current of 5 nA and a 1 μm beam diameter. Contents of other elements with atomic number higher than eight were found to be below the detection limits. The content of H_2O was not determined directly due to the scarcity of pure material. It was calculated by stoichiometry for the formula based on 11 O *apfu*, by analogy with the isostructural mineral martyrite. A good agreement be-

tween the calculated value for H_2O and the deficiency in the total of the averaged electron microprobe analysis (Tab. 1) supports the correctness of this assumption.

The empirical formula of karpenkoite, calculated on the basis of 11 O *apfu*, is $(Co_{2.06}Zn_{0.72}Ni_{0.13}Mn_{0.09}Ca_{0.02}Cu_{0.02}Mg_{0.01})_{\Sigma 3.05}V_{1.98}O_7(OH)_2 \cdot 2H_2O$. The idealized formula $Co_3(V_2O_7)(OH)_2 \cdot 2H_2O$ requires CoO 48.81, V_2O_5 39.45, H_2O 11.74, total 100 wt. %.

5. Raman spectroscopy

Our Raman studies included the collection of the spectra of karpenkoite and, for comparison, its zinc analogue martyrite, $Zn_3(V_2O_7)(OH)_2(H_2O)_2$. The sample of the latter (from the collection of Anatoly Kasatkin; confirmed by electron microprobe and powder X-ray diffraction) originates from the mineral's type locality, the Blue Cap mine, San Juan Co., Utah.

The Raman spectra of both minerals were obtained using an EnSpectr R532 spectrometer (Department of Mineralogy, Moscow State University) utilizing a green laser (532 nm) at room temperature. The output power of the laser beam was about 4 mW. Spectra were processed by the EnSpectr expert mode program in the range 100 to 4000 cm^{-1} with the use of a 1800 mm^{-1} holographic diffraction grating and a spectral resolution of 5–8 cm^{-1} . The diameter of the focal spot on each sample was about 15 μm . The spectra were obtained for polycrystalline aggregates of both minerals.

The Raman spectra of karpenkoite and martyrite are quite similar (Electronic Supplement). Tentative assignment of Raman bands of these minerals was done following Schwendt and Joniaková (1975), Nakamoto (1986), Harcastle and Wachs (1991), Obbade et al. (2004) and Frost et al. (2011). The broad band with a maximum in the region $3450\text{--}3530 \text{ cm}^{-1}$ corresponds to O–H stretching vibrations. The relatively weak, broad band with maximum at $1660\text{--}1670 \text{ cm}^{-1}$ is assigned to

Tab. 1 Chemical composition of karpenkoite (wt. %)

Constituent	Mean ($n = 12$)	Range	SD	Probe standard
MgO	0.05	0.00–0.47	0.154	Olivine
CaO	0.26	0.00–0.70	0.24	Cr-augite USNM**
MnO	1.39	0.00–3.53	1.28	Mn
CoO	33.22	23.05–45.23	8.08	Co
NiO	2.02	0.98–3.85	0.91	Ni
CuO	0.28	0.00–0.82	0.26	Cu
ZnO	12.66	1.58–21.59	7.52	Zn_2SiO_4
V_2O_5	38.70	37.48–39.92	0.68	V
H_2O calc.	11.61*			
Total	100.19			

SD – standard deviation

*calculated by stoichiometry

** Smithsonian National Museum of Natural History (Washington, D.C., USA)

bending vibrations of H₂O molecules. Note that this band is, however, rather broad for typical bands attributed to H–O–H bending modes. The broadening could be explained by overlap with an overtone related to the most intense band of V⁵⁺–O stretching vibrations in the region 800–860 cm⁻¹. A very strong band centered at 823 cm⁻¹ in the Raman spectrum of karpenkoite and that at 844 cm⁻¹ in the spectrum of martyite are undoubtedly due to symmetric stretching vibrations of V⁵⁺O₃ units. Bands in the region 300–500 cm⁻¹ are assigned to V⁵⁺O₃ bending vibrations and bands with frequencies lower than 300 cm⁻¹ may be related to lattice modes. The lack of distinct bands in the regions 1000–1500 and 1700–3000 cm⁻¹ indicates the absence of H₃O⁺ and groups with C–O, C–H, N–O, N–H and B–O bonds in karpenkoite and martyite.

Tab. 2 Powder X-ray diffraction data of karpenkoite

Karpenkoite				Martyite*				
<i>I</i> _{obs}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{calc} **	<i>I</i> _{calc}	<i>d</i> _{calc}	h	k	<i>l</i>
100	7.15	7.234	100	100	7.179	0	0	1
18	5.19	5.210	16	4	5.267	0	1	0
25	4.20	{ 4.228	9	17	{ 4.247	1	0	1
21	3.59	{ 4.228	8	4	{ 4.247	0	1	1
		{ 3.617	3	6	{ 3.590	0	0	2
54	2.95	{ 2.971	22	49	{ 3.041	1	1	0
21	2.77	{ 2.971	27	14	{ 2.966	0	1	2
36	2.60	{ 2.777	14	30	{ 2.966	1	0	2
33	2.44	{ 2.605	30	30	{ 2.634	2	0	0
17	2.30	{ 2.451	29	32	{ 2.634	2	0	1
11	2.17	{ 2.451	2	8	{ 2.472	0	2	1
17	2.10	{ 2.313	9	4	{ 2.320	1	1	2
		{ 2.188	3	4	{ 2.179	1	0	3
		{ 2.188	1	13	{ 2.179	0	1	3
		{ 2.114	13	13	{ 2.123	2	0	2
		{ 2.114	1	5	{ 2.123	0	2	2
6	1.886	1.881	3	3	1.918	1	2	1
2	1.800	1.808	4	4	1.881	1	1	3
11	1.761	{ 1.770	9	17	{ 1.795	0	0	4
10	1.721	{ 1.770	8	14	{ 1.771	2	0	3
		{ 1.729	7	1	{ 1.771	0	2	3
		{ 1.729	7	14	{ 1.741	1	2	2
1	1.555	{ 1.566	2	3	{ 1.741	2	1	2
13	1.503	{ 1.566	2	7	{ 1.705	0	3	1
		{ 1.504	18	14	{ 1.577	3	0	2
		{ 1.486	7	7	{ 1.577	0	3	2
		{ 1.486	14	15	{ 1.520	2	2	0
					1.488	2	2	1
					1.483	2	0	4
					1.483	0	2	4

d values quoted in Å

Range: 3–30° 2θ, MoK_α radiation

*Kampf and Steele (2008)

**Calculated based on the model of martyite structure with Co instead of Zn

6. Powder X-ray diffraction data

Single-crystal X-ray diffraction studies of karpenkoite could not be carried out because of the imperfection of its single crystals, which are very thin and typically divergent lamellae. For these reasons a Gandolfi-like scans were used to obtain powder diffraction data (Tab. 2) from an aggregate of randomly oriented crystals mounted on a glass fiber and scanned using an Agilent Technologies Supernova single-crystal diffractometer with a Mo micro-focus X-ray tube (50 kV, 0.8 mA), which provides a 140 μm focused brilliant beam. The diffracted X-rays were collected using a Dectris Pilatus 200K detector. Raw diffraction data were processed using CrysAlis software (Agilent Technologies 2014). The data were further processed by the LeBail whole-pattern decomposition in Jana2006 software (Petříček et al. 2006, 2014), using the known structure model for the isostructural mineral martyite. Refined values of the unit cell parameters were corrected for correlations after Bérar and Lelann (1991), and are (for the trigonal space group *P* $\bar{3}m1$) *a* = 6.016(4), *c* = 7.234(6) Å, with *V* = 226.7(2) Å³ and *Z* = 1.

7. Discussion

Despite of absence of single-crystal X-ray diffraction data, there is no doubt that karpenkoite Co₃(V₂O₇)(OH)₂·2H₂O is the cobalt analogue of martyite Zn₃(V₂O₇)(OH)₂·2H₂O (Kampf and Steele 2008) and its synthetic analogue (Zavaliy et al. 1997). Comparative characteristics of karpenkoite and martyite are given in Tab. 3. We based our conclusions regarding the isotypism of these minerals primarily on the fact that the stereochemistry of Zn²⁺ and Co²⁺ in oxysalts is similar (effective ionic radii are 0.74 Å and 0.75 Å for ^[6]Zn²⁺ and ^[6]Co²⁺, respectively – Shannon 1976). In particular, the stoichiometry of both minerals is identical and their crystal morphology and physical

properties (including Raman spectra and optical data) are very close. The most convincing argument is a very good agreement between measured intensities of the reflections in the powder X-ray diffraction pattern of karpenkoite and calculated intensities of reflections for martyite (Tab. 2). A comparison with hexagonal engelhauptite and monoclinic volborthite ($C2/m$), structurally related to martyite (Kampf and Steele 2008; Pekov et al. 2015), indicates much poorer correspondence. Based on these similarities, we infer that karpenkoite adopts the same structure as martyite.

Although crystals of karpenkoite on the holotype specimen exhibit considerable inhomogeneity in their Co:Zn ratio, all showed dominance of Co over Zn in all analyzed points. The cobalt-richest and zinc-poor point has the composition $(\text{Co}_{2.80}\text{Zn}_{0.09}\text{Ni}_{0.07}\text{Ca}_{0.05}\text{Mn}_{0.02}\text{Cu}_{0.02})_{\Sigma 3.05}\text{V}_{1.98}\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, whereas the Co-poor and Zn-richest point has the composition $(\text{Co}_{1.46}\text{Zn}_{1.15}\text{Mn}_{0.21}\text{Ni}_{0.20})_{\Sigma 3.02}\text{V}_{1.99}\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. On other samples from the Little Eva mine studied by us, karpenkoite and martyite occur together forming a nearly continuous solid-solution series (Fig. 4).

Note that the crystal structures of two copper divanadate minerals, monoclinic ($C2/m$) volborthite $\text{Cu}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (Lafontaine et al. 1990; Kashaev et al. 2008) and hexagonal engelhauptite $\text{KCu}_3(\text{V}_2\text{O}_7)(\text{OH})_2\text{Cl}$ (Pekov et al. 2015), are topologically identical (with regard to the topology of the structural units) to that of martyite and, presumably, karpenkoite, but volborthite and engelhauptite differ from one another in some crystal-chemical features. Volborthite adopts monoclinic symmetry due to the significant Jahn–Teller distortion of one of the two symmetrically non-equivalent CuO_6 octahedra. Engelhauptite contains the contact ion pairs K^+Cl^- in channels of the framework $[\text{Cu}^{2+}_3(\text{V}_2\text{O}_7)(\text{OH})_2]^{0-}$ instead of H_2O molecules as in volborthite, martyite and karpenkoite.

Tab. 3 Comparative data for karpenkoite and martyite

Mineral	Karpenkoite	Martyite*
End-member formula	$\text{Co}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	$\text{Zn}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$
Average divalent metal content (for the holotype samples of each mineral)	$\text{Co}_{2.06}\text{Zn}_{0.72}\text{Ni}_{0.13}\text{Mn}_{0.09}\text{Ca}_{0.02}\text{Cu}_{0.02}\text{Mg}_{0.01}$	$\text{Zn}_{2.66}\text{Co}_{0.15}\text{Ca}_{0.05}$
Crystal system	Trigonal	Trigonal
Space group	$P\bar{3}m1$	$P\bar{3}m1$
a , Å	6.016(4)	6.0818(4)
c , Å	7.234(6)	7.1793(10)
V , Å ³	226.7(2)	229.97(4)
Z	1	1
Strongest lines of the X-ray powder-diffraction pattern: d , Å (I , %)	7.15(100)	7.211(100)
	4.20(25)	2.968(50)
	2.95(54)	2.628(35)
	2.60(36)	2.470(40)
	2.44(33)	1.485(25)
Wavenumbers of main bands in the Raman spectrum, cm ⁻¹	3500	3475
	1670	1660
	823	844
	474	483
	443	440
	312	319
	253	258
Color	Orange	Yellow-orange to red-orange
Optical data	Uniaxial (+) $\omega = 1.827(8)$ $\epsilon = 1.843(8)$	Uniaxial (+) $\omega = 1.797(3)$ $\epsilon = 1.806(3)$
	Density, g cm ⁻³	3.416 (calc.)
References	This work	Kampf and Steele (2008); Raman data – this work

*The unit-cell parameters of the synthetic analogue of martyite are: $a = 6.05098(5)$ Å, $c = 7.19498$ Å, $V = 228.15$ Å³; Zavaliı et al. (1997)

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Electronic supplementary material. Supplementary chemical analyses of karpenkoite and martyite, as well as their Raman spectra are available online at the Journal web site (<http://dx.doi.org/10.3190/jgeosci.199>).

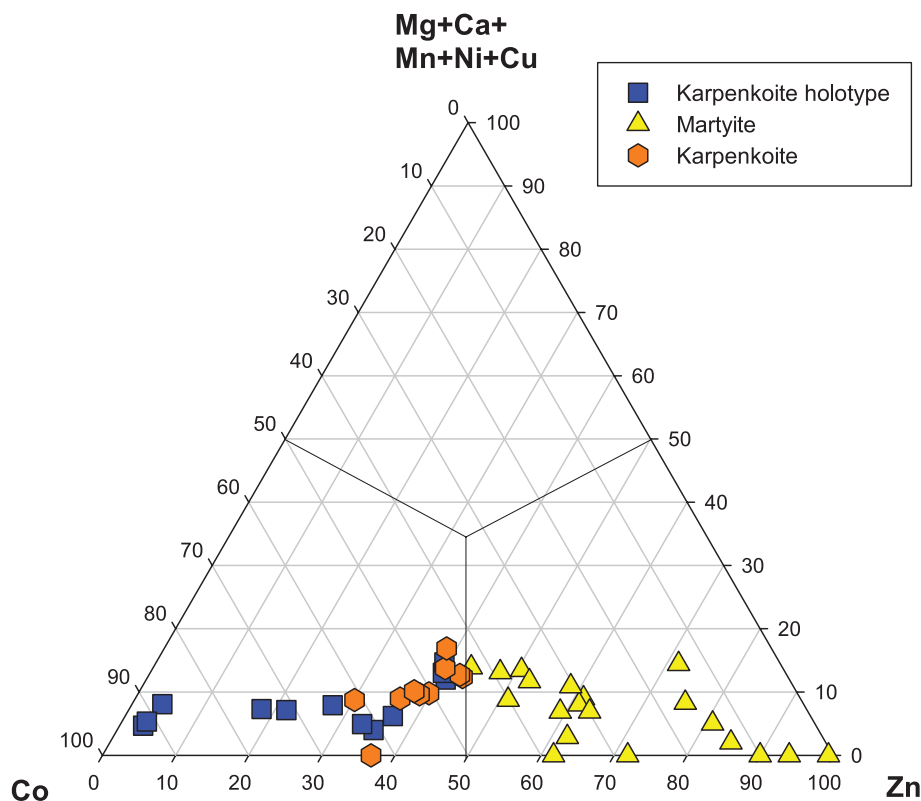


Fig. 4 Ratios of species-defining M^{2+} cations in members of the karpenkoite–martyite solid-solution series from the Little Eva mine, Grand Co., Utah, USA.

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