

Engelhauptite, $\text{KCu}_3(\text{V}_2\text{O}_7)(\text{OH})_2\text{Cl}$, a new mineral species from Eifel, Germany

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Abstract A new mineral engelhauptite, $\text{KCu}_3(\text{V}_2\text{O}_7)(\text{OH})_2\text{Cl}$, was found within cavities in nepheline basalts at the Auf'm Kopp quarry ("Schlackenkegel der Höhe 636 südöstlich Neroth"), Daun, Eifel region, Rheinland-Pfalz, Germany. Associated minerals are volborthite, allophane, malachite, tangeite and chrysocolla; earlier minerals belonging to the primary, high-temperature parageneses are augite, mica of the phlogopite–oxyphlogopite series, sanidine, nepheline, leucite, fluorapatite and magnetite. Engelhauptite occurs as spherulites (up to 0.2 mm in diameter) and bunches consisting of rough spindle-shaped crystals elongated parallel to [0001]. The crystals are up to 0.12 mm long and up to 0.04 mm thick. Individual grains of engelhauptite are transparent, whereas their aggregates are translucent. The mineral is yellow-brown to brown, typically with an olive green hue. The luster is vitreous. Engelhauptite is brittle, cleavage is not observed, fracture is uneven. $D_{\text{calc}} = 3.86 \text{ g cm}^{-3}$. Engelhauptite is optically uniaxial (+), $\omega = 1.978(4)$, $\varepsilon =$

2.021(4). Chemical data (wt.%, electron-microprobe, H_2O by difference) are as following: K_2O 9.63, FeO 0.05, NiO 0.29, CuO 46.11, Al_2O_3 0.24, V_2O_5 34.92, SO_3 0.79, Cl 5.94, $\text{H}_2\text{O}_{\text{calc}}$ 3.37, $\text{O}=\text{Cl}_2$ -1.34, total 100.00. The empirical formula, based on 10 ($\text{O} + \text{OH} + \text{Cl}$) *apfu*, is $\text{K}_{1.05}(\text{Cu}_{2.97}\text{Al}_{0.02}\text{Ni}_{0.02})_{\Sigma 3.01}(\text{V}_{1.97}\text{S}_{0.05})_{\Sigma 2.02}\text{O}_{7.23}(\text{OH})_{1.91}\text{Cl}_{0.86}$. Engelhauptite is hexagonal, $P6_3/mmc$, $a = 5.922(2)$, $c = 14.513(5) \text{ Å}$, $V = 440.78(3) \text{ Å}^3$ and $Z = 2$. The eight strongest reflections of the powder X-ray diffraction pattern [$d, \text{Å} / (hkl)$] are: 7.32(98) (002), 4.224(17) (102), 2.979(100) (104, 110), 2.759(19) (112), 2.565(18) (200), 2.424(18) (202), 1.765(16) (206) and 1.481(14) (208, 220). The crystal structure of engelhauptite has been solved from the single-crystal X-ray diffraction data and refined to $R = 0.090$ on the basis of 135 unique observed reflections. The structure is based upon the $[\text{Cu}^{2+}_3(\text{V}_2\text{O}_7)(\text{OH})_2]^0$ framework formed by the linkage of deficient brucite-like layers of Jahn-Teller distorted CuO_6 octahedra ($\varphi = \text{O}, \text{OH}$) via divanadate V_2O_7 groups. The framework contains large channels occupied by K^+ cations and Cl^- anions. Engelhauptite is closely related to volborthite, $\text{Cu}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, and can be considered as its analogue resulting from the replacement of H_2O molecules by the equal amounts of K^+ and Cl^- ions. The mineral is named in honour of the German amateur mineralogist and mineral collector Bernd Engelhaupt (born 1946).

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Introduction

There are 20 copper vanadates known to date as valid mineral species. Among them, 13 are H-free and have been found in hot active fumaroles at the Izalco (El Salvador) and Tolbachik (Kamchatka, Russia) volcanoes: averievite, $\text{Cu}_6\text{O}_2(\text{VO}_4)_2\text{Cl}_2 \cdot n(\text{Cs}, \text{K}, \text{Rb}) \text{Cl}$, blossomite, $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$, fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, howardevansite, $\text{NaCuFe}^{3+}_2(\text{VO}_4)_3$,

leningradite, $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$, lyonsite, $\text{Cu}_{3+x}(\text{Fe}^{3+}_{4-2x}\text{Cu}_{2x})(\text{VO}_4)_6$ (with $0 \leq x \leq 1$), mcbirneyite, $\text{Cu}_3(\text{VO}_4)_2$, stoiberite, $\text{Cu}_5\text{O}_2(\text{VO}_4)_2$, ziesite $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ (Anthony et al. 2000), and recently described pseudolyonsite, $\text{Cu}_3(\text{VO}_4)_2$ (Zelenski et al. 2011), starovaite, $\text{KCu}_5\text{O}(\text{VO}_4)_3$, yaroshevskite, $\text{Cu}_9\text{O}_2(\text{VO}_4)_4\text{Cl}_2$, and grigorievite, $\text{Cu}_3\text{Fe}^{3+}_2\text{Al}_2(\text{VO}_4)_6$, (Pekov et al. 2013a, b, 2014). The H-bearing copper vanadates include mottramite, $\text{PbCuVO}_4(\text{OH})$, namibite, $\text{Cu}(\text{BiO})_2\text{VO}_4(\text{OH})$, sengierite, $\text{Cu}_3(\text{UO}_2)(\text{VO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, tangeite, $\text{CaCuVO}_4(\text{OH})$, vesigneite, $\text{BaCu}_3(\text{VO}_4)_2(\text{OH})_2$, volborthite, $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (see for all: Anthony et al. 2000), and turanite, $\text{Cu}_5(\text{VO}_4)_2(\text{OH})_4$ (Sokolova et al. 2004). Unlike H-free vanadates, these minerals occur in low-temperature, supergene environments, commonly in oxidation zones of copper-containing ore deposits.

Herein we describe engelhauptite, a new copper vanadate with the idealized formula $\text{KCu}_3(\text{V}_2\text{O}_7)(\text{OH})_2\text{Cl}$ found in the late mineral association related to the young alkaline lavas in the Eifel paleovolcanic region, Germany.

The mineral was named engelhauptite (Cyrillic: энгельгауптит) in honour of the amateur mineralogist and mineral collector Bernd Engelhaupt (born 1946) from Gerolstein, Rheinland-Pfalz, Germany, for his contributions to the mineralogy of the Eifel region. Both the new mineral and its name have been approved by the IMA CNMNC, IMA2013–009. The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, under the catalogue number 94124.

Occurrence and general appearance

The type locality of engelhauptite is an outcrop of volcanic rocks at the Auf'm Kopp or Kahlenberg quarry, also known as “Schlackenkegel der Höhe 636 südöstlich Neroth”, Daun, Oberstadtfeld Municipality, Eifel Mountains, Rheinland-Pfalz (Rhineland-Palatinate), Germany. The specimens with the mineral were collected by Bernd Engelhaupt, who transferred them to the authors for study.

The quarry was operated for road material and is now abandoned. The major rocks at the quarry are nepheline basalts, leucitic nephelinite, lapilli tuffs and agglutinates, which all are the products of Late Pleistocene volcanic activity (Leu 1995).

Engelhauptite was found within cavities in the nepheline basalt lava. It is one of the last minerals of the assemblage closely associated with volborthite (Fig. 1a) and allophane. Together with engelhauptite, these minerals overgrew crystalline crusts consisting mainly of augite, sanidine, nepheline, leucite, mica of the phlogopite–oxyphlogopite series and magnetite obviously belonging to the primary, high-temperature paragenesis. In the neighbouring cavities, other late hydrated

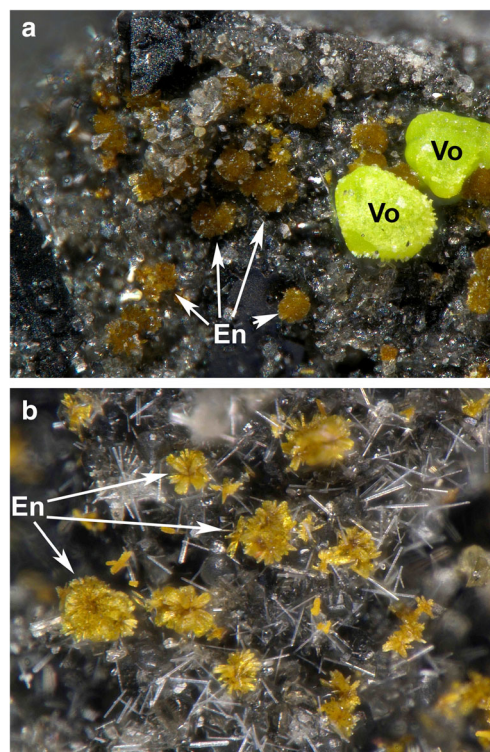


Fig. 1 Spherulites (up to 0.1 mm in diameter) and bunches of engelhauptite (En) with balls of volborthite (Vo) **a** on a crystal crust mainly consisting of black augite and colourless sanidine; **b** on a crust composed of nepheline (colourless acicular crystals) and leucite (small colourless equant, roundish crystals); photos S. Wolfsried

copper oxysalts are observed, such as malachite, tangeite and chrysocolla.

Engelhauptite occurs as spherulites and bunches of rough spindle-shaped crystals elongated parallel to $[0001]$. The aggregates are usually divergent, with a blocky surface and round cross-sections (Figs. 1 and 2). In rare cases, coarse hexagonal cross-sections are observed. The major forms of the divergent crystals are most probably the $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ prisms. In some cases, crystals are terminated by the $\{0001\}$ pinacoids (Fig. 2b). Some individual split crystals are up to 0.12 mm long and up to 0.04 mm thick. However, their typical dimensions are 0.01×0.05 mm; spherulites are up to 0.2 mm in diameter.

Physical properties and optical data

Engelhauptite is yellow-brown to brown, typically with an olive green hue. The streak is yellow. The luster is vitreous. The mineral is transparent in individual grains and translucent in aggregates. Engelhauptite is brittle. Cleavage or parting has not been observed. The fracture is uneven. Hardness and density could not be measured because of the very small size of individual grains and the porosity of the aggregates. The density calculated based on the empirical formula is 3.86 g cm^{-3} .

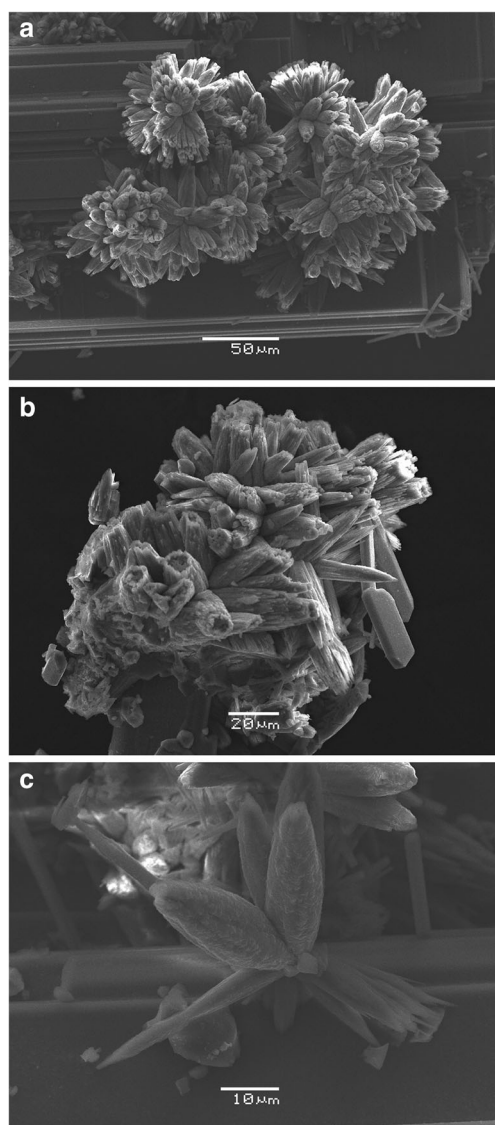


Fig. 2 Secondary electron (SE) SEM images showing crystals and aggregates of engelhauptite: **a**, **c** on phlogopite, **b** on augite

Engelhauptite is optically uniaxial (+), $\omega=1.978(4)$, $\varepsilon=2.021(4)$. Pleochroism is weak, with the absorption scheme: ω (brownish yellow) $>$ ε (light yellow).

Infrared spectroscopy

The infrared (IR) absorption spectrum of engelhauptite was measured on a powdered sample mixed with anhydrous KBr and pelletized. The pellet was analyzed using an ALPHA FTIR spectrometer (Bruker Optics) in Institute of Problems of Chemical Physics, Chernogolovka. The IR spectrum of an analogous pellet of pure KBr was used as a reference. Background and sample spectra were obtained from 16 scans with a nominal resolution of 4 cm^{-1} .

The IR spectrum of engelhauptite (Fig. 3) is unique. Absorption bands in the spectrum and their assignments (cm^{-1} ; s – strong band, w – weak band, sh – shoulder) are as follows: 3482w, 3312w, 2810 (O–H stretching vibrations), 1150sh, 1060w, 990sh, (S–O stretching vibrations), 964, 901, 838 s, 779 s, 735sh (V–O stretching vibrations combined with bending vibrations of $\text{Cu}\cdots\text{OH}$ groups), 570sh, 545, 520sh, 471 (O–V–O bending vibrations of $\text{V}_2\text{O}_7^{4-}$ anions). Bands of V–O–V bending vibrations of $\text{V}_2\text{O}_7^{4-}$ anions could not be observed in the operating frequency range (above 360 cm^{-1}) because effective reduced mass of corresponding normal vibrations (with strong displacements heavy V atoms) is too high, and their effective force constant is lower than those for O–V–O bending vibrations involving shorter V–O bonds.

According to the correlation $\nu\text{ (cm}^{-1}\text{)}=3592-304\cdot 10^9\cdot \exp[-d(\text{O}\cdots\text{O})/0.1321]$ established by Libowitzky (1999) for hydrogen bonds formed by OH groups and H_2O molecules, the distance $\text{O}\cdots\text{OH}$ of 2.88 Å in engelhauptite corresponds to the O–H-stretching frequency 3492 cm^{-1} . This value is in a good agreement with the observed value 3489 cm^{-1} . We believe that hydrogen bond with Cl can be excluded from consideration, because Cl is a weaker acceptor than O, and corresponding O–H-stretching band would be present in the frequency region above 3492 cm^{-1} .

The assignment of the band at 3312 cm^{-1} is ambiguous. Based on some deficiency of Cl in the empirical formula, we suggest that there could be a minor admixture of OH at the Cl site. The wavenumber 3312 cm^{-1} corresponds to the distance $\text{O}\cdots\text{OH}$ of 2.75 Å. The distance $\text{O}2\cdots\text{Cl}$ in engelhauptite is equal to 2.91 Å. Consequently, under the above assumption, the subsite of the admixed OH group could be expected at the distance of 0.16 Å from the subsite of Cl.

The band at 2810 cm^{-1} would correspond to the strong hydrogen bond formed by OH group or H_2O molecule with the respective distance $\text{O}\cdots\text{O}$ of 2.6 Å. However, such a short distance between the O atoms is absent in engelhauptite.

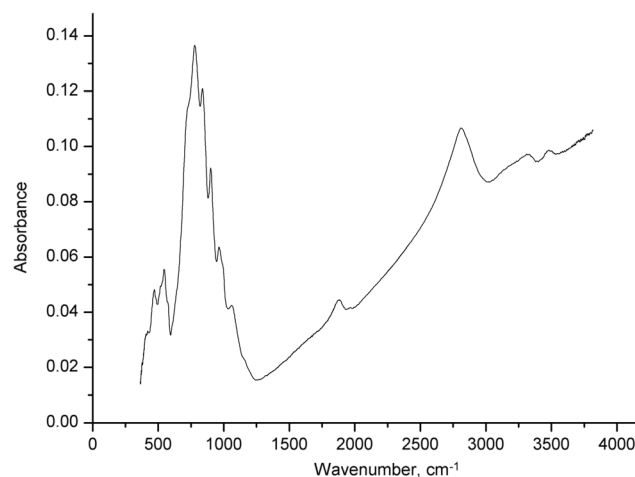


Fig. 3 The infrared (IR) absorption spectrum of engelhauptite

Therefore, we suggest that this band could be assigned to OH groups of the acid anion $\text{HV}_2\text{O}_7^{3-}$ formed as a result of proton transfer according to the dynamic acid–base equilibrium $\text{OH}^- + \text{V}_2\text{O}_7^{4-} \leftrightarrow \text{O}^{2-} + \text{HV}_2\text{O}_7^{3-}$. The expected fraction of protonated O atoms is low. For instance, if 0.3 *apfu* H is distributed among six O1 atoms, the degree of protonation of the O1 site is 5 % only, which would not be detectable by the X-ray diffraction analysis. A relatively weak band at 1869 cm^{-1} confirms the possible presence of acidic OH groups formed due to the above dynamic acid–base equilibrium.

The absence of absorption bands in the range $1500\text{--}1700\text{ cm}^{-1}$ indicates that any substantial amounts of H_2O molecules (both adhesive and structural) are absent in the sample examined.

A series of very weak, narrow bands in the ranges $3500\text{--}3800$, $1300\text{--}1800\text{ cm}^{-1}$ and below 460 cm^{-1} are due to atmospheric water vapor. Bands of B-, C- and N-bearing groups are absent.

Chemical composition

Chemical data for engelhauptite were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Local Methods of Matter investigation, Faculty of Geology, Moscow State University). The WDS mode was used, with an acceleration voltage of 20 kV, a beam current of 20 nA, and a beam diameter of 3 μm . The standards used are: microcline (K, Al), CuFeS_2 (Fe, Cu), Ni (Ni), vanadinite (V, Cl), and BaSO_4 (S). The H_2O content was not determined because of the paucity of the available material, but was calculated by difference and is in good agreement with the data obtained from the single-crystal structure refinement (see below).

The average chemical composition of engelhauptite (wt.%, ranges for 10 electron microprobe analyses are in parentheses) is: K_2O 9.63 (9.21–10.02), FeO 0.05 (0.00–0.19), NiO 0.29 (0.08–0.46), CuO 46.11 (45.04–46.88), Al_2O_3 0.24 (0.07–0.38), V_2O_5 34.92 (33.23–36.07), SO_3 0.79 (0.42–1.09), Cl 5.94 (5.32–6.34), $\text{H}_2\text{O}_{\text{calc}}$ 3.37, $\text{O}=\text{Cl}_2$ -1.34, total 100.00. Contents of other elements with atomic numbers higher than six are below detection limits.

The empirical formula, calculated on the basis of 10 anions ($\text{O} + \text{OH} + \text{Cl}$) *p f u*, is: $\text{K}_{1.05}(\text{Cu}_{2.97}\text{Al}_{0.02}\text{Ni}_{0.02})_{\Sigma 3.01}(\text{V}_{1.97}\text{S}_{0.05})_{\Sigma 2.02}\text{O}_{7.23}(\text{OH})_{1.91}\text{Cl}_{0.86}$. The idealized formula is $\text{KCu}_3(\text{V}_2\text{O}_7)(\text{OH})_2\text{Cl}$, which requires K_2O 9.18, CuO 46.51, V_2O_5 35.45, Cl 6.91, H_2O 3.51, $\text{O}=\text{Cl}$ -1.56, total 100.00 wt.%.

X-ray crystallography and crystal structure

Powder X-ray diffraction data for engelhauptite (Table 1) were collected using a STOE IPDS II diffractometer equipped with an Image Plate area detector, using the Gandolfi method ($\text{MoK}\alpha$ -radiation; detector-to-sample distance: 200 mm). The unit cell parameters calculated from the powder data using a WinX^{pow} Software (2002) are: $a=5.928(4)$, $c=14.54(1)\text{ \AA}$, $V=442.6(9)\text{ \AA}^3$.

A very thin plate-like crystal of the mineral was mounted on a Bruker APEX II DUO X-ray diffractometer operated at 50 kV and 40 mA and equipped with a micro-focus X-ray tube with the Mo anode. The data were integrated and corrected for absorption using a multi-scan type model with the Bruker

Table 1 Powder X-ray diffraction data for engelhauptite

I_{obs}	$d_{\text{obs}}, \text{\AA}$	I_{calc}^a	$d_{\text{calc}}, \text{\AA}^b$	$h\ k\ l$
98	7.32	28	7.257	002
3	4.849	12	4.836	101
17	4.224	3	4.188	102
8	3.632	22	3.628	004
3	3.528	4	3.519	103
100	2.979	100, 24	2.962, 2.961	104, 110
19	2.759	49	2.742	112
18	2.565	26	2.564	200
18	2.424	45	2.418	202
8	2.299	1	2.294	114
11	2.272	6	2.266	203
3	2.200	0.5	2.188	106
6	2.102	5	2.094	204
2	1.934	1	1.922	205
5	1.883	11, 4	1.873, 1.873	116, 212
16	1.765	30	1.760	206
8	1.710	19, 2	1.710, 1.710	214, 300
2	1.665	5	1.664	302
2	1.544	2, 1	1.547, 1.547	118, 304
14	1.481	13, 16	1.481, 1.481	208, 220
2	1.426	5, 0.5, 0.5	1.451, 1.416, 1.416	222, 217, 311
3	1.326	8	1.324	314
3	1.307	5	1.303	1.1.10
3	1.283	4	1.282	400
3	1.266	4, 1, 2	1.263, 1.263, 1.263	2.0.10, 226, 402
1	1.211	1	1.209	404
1	1.177	2	1.177	1.0.12
1	1.147	5	1.147	228
2	1.131	2	1.133	406
1	1.120	3	1.119	324
1	1.049	3	1.047	408

^a Only reflections with $I_{\text{calc}} \geq 0.5$ are taken into account

^b Calculated for the unit cell parameters obtained from single-crystal data

Table 2 Crystallographic data and refinement parameters for engelhauptite

Crystal data	
Temperature	293 K
Radiation, wavelength	MoK α , 0.71073 Å
Crystal system	hexagonal
Space group	$P6_3/mmc$
Unit-cell dimensions a, c (Å)	5.922 (2), 14.513 (5)
Unit-cell volume (Å ³)	440.8 (3)
Z	2
Absorption coefficient (mm ⁻¹)	9.96
Crystal size (mm ³)	0.04×0.04×0.009
Data collection	
Θ range	3.97–25.10°
h, k, l ranges	−6→4, −6→7, −17→17
Total reflections collected	1495
Unique reflections (R_{int})	171 (0.057)
Unique reflections $F > 4\sigma(F)$	135
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting coefficients a, b	0.0550, 51.2071
Data/restraints/parameters	135/18/28
$R_1 [F > 4\sigma(F)], wR_2 [F > 4\sigma(F)]$	0.090, 0.193
R_1 all, wR_2 all	0.112, 0.206
Goodness-of-fit on F^2	1.187
Largest diff. peak and hole, $e \text{ Å}^{-3}$	1.480, −1.277

programs *APEX* and *SADABS*. More than a hemisphere of X-ray diffraction data was collected with the frame widths of 0.3° in ω , and with 250 s spent counting for each frame. The structure was solved in the space group $P6_3/mmc$ by direct methods, which allowed to locate positions of Cu, V, K and Cl; the positions of the O atoms were identified from the analysis of Fourier difference electron-density maps. The crystal structure was refined to $R_1=0.090$ by means of the SHELX-97 package (Sheldrick 2008) on the basis of 135 independent reflections with $I > 4\sigma(I)$. The crystals of engelhauptite are of small size and poor quality (there were no detectable diffraction

Table 4 Selected bond lengths (Å) in the crystal structure of engelhauptite

Cu–OH	1.92 (1)×2
Cu–O1	2.23 (2)×4
V–O1	1.66 (2)×3
V–O2	1.758 (8)
K–O1	2.95 (2)×6
K–Cl	3.20 (1)×3

maxima at $2\Theta > 50^\circ$), which did not allow us to resolve all the details of its crystal structure. The poor quality of the X-ray diffraction data is manifested in the high R_1 index and the high standard deviations of interatomic distances. Structure refinement revealed positional disorder at the Cl site, which has the site-occupancy factor (s.o.f.) of 1/3. For the K and O2 sites, soft restraints were applied in order to keep their displacement parameters at physically reasonable values (it is noteworthy that the O2 atoms is bridging between two adjacent VO₄ tetrahedra). Thirteen most disagreeable reflections were omitted from the final refinement to improve the refinement parameters. Crystal data and structure refinement parameters are given in Table 2, atom coordinates and displacement parameters in Table 3 and selected interatomic distances in Table 4.

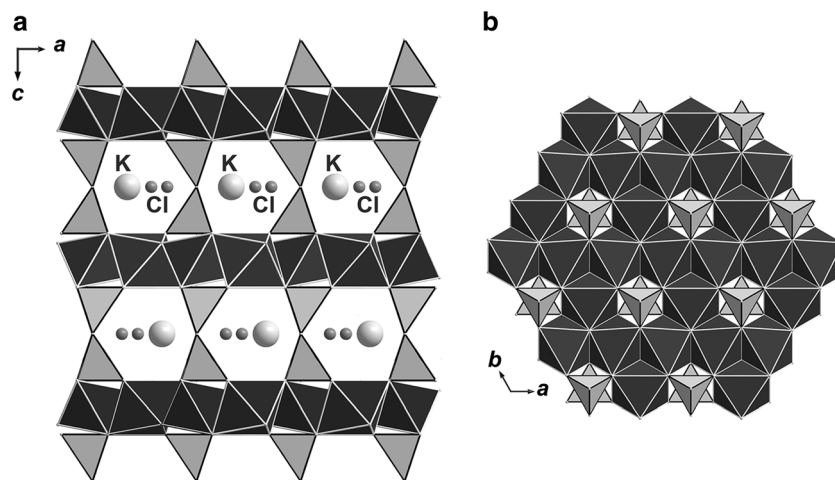
The crystal structure of engelhauptite (Fig. 4a) contains one symmetrically unique Cu position (Table 3) coordinated by four O^{2−} and two OH[−] anions. The octahedral coordination of the Cu²⁺ cation is rather untypical and displays a [2+4] distortion of coordination geometry instead of the more usual [4+2] distortion (see comments below). The CuO₄ (OH)₂ polyhedra share common edges and corners to form sheets (Fig. 4b), which can be considered as brucite-like sheets with 1/4 of octahedral sites vacant. There is one symmetrically independent V⁵⁺ cation in the structure, which is tetrahedrally coordinated by four O^{2−} anions. The VO₄ tetrahedra are located above and below vacancies in the copper hydroxide sheets. The tetrahedra from two adjacent sheets share common O2 atoms, forming (V₂O₇) divanadate groups to form electroneutral [Cu²⁺₃(V₂O₇) (OH)₂]⁰ framework with large cavities occupied by K⁺ and Cl[−] ions. The V–O2 bond of 1.752(8) Å is significantly elongated compared to the three

Table 3 Atom coordinates and displacement parameters (Å²) for the crystal structure of engelhauptite

Atom	Wyckoff site	x/a	y/b	z/c	U _{eq}	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Cu	6g	1/2	1/2	0	0.027 (1)	0.034 (2)	= U ₁₁	0.014 (2)	−0.003 (1)	= −U ₂₃	0.018 (2)
V	4e	0	0	0.1288 (4)	0.028 (2)	0.040 (3)	= U ₁₁	0.003 (3)	0	0	0.020 (1)
K	2c	1/3	2/3	1/4	0.018 (3)	0.024 (4)	= U ₁₁	0.004 (5)	0	0	0.012 (2)
OH	4f	1/3	2/3	−0.060 (2)	0.015 (6)	0.019 (9)	= U ₁₁	0.008 (12)	0	0	0.009 (5)
O1	12k	0.153 (2)	−0.153 (2)	0.092 (1)	0.044 (5)	0.045 (8)	= U ₁₁	0.047 (10)	0.015 (6)	= −U ₂₃	0.03 (1)
O2	2b	0	0	1/4	0.09 (2)	0.13 (3)	= U ₁₁	0.01 (2)	0	0	0.06 (2)
Cl ^a	6h	−0.716 (3)	−0.433 (6)	3/4	0.08 (2)	0.13 (4)	0.02 (2)	0.049 (16)	0	0	0.010 (9)

^a s.o.f. = 1/3

Fig. 4 Crystal structure of engelhauptite. **a** General projection along the *b* axis. Large elliptical channels in neutral $[\text{Cu}^{2+}_3(\text{V}_2\text{O}_7)(\text{OH})_2]^0$ framework $[\text{CuO}_4(\text{OH})_2=\text{black}, \text{V}_2\text{O}_7=\text{grey}]$ are occupied by K^+ cations (light-grey circles) and Cl^- anions (dark-grey circles). **b** Polyhedral representation of the structure of engelhauptite along the *c* axis



V-O1 bonds of 1.62(3) Å. Similar elongation of the V-O bonds to the O atoms bridging in the V_2O_7 divanadate groups is observed in the crystal structures of volborthite (Basso et al. 1988) and martyite, $\text{Zn}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (Kampf and Steele 2008). The K^+ atom has a ninefold coordination by six O and three Cl atoms (taking into account the disorder observed for the Cl sites).

Discussion

The crystal structure of engelhauptite is closely related to that of volborthite, $\text{Cu}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (Basso et al. 1988). Both structures are based upon the same copper-hydroxy-vanadate framework with the chemical composition $[\text{Cu}^{2+}_3(\text{V}_2\text{O}_7)(\text{OH})_2]$. In volborthite, the framework cavities are occupied by H_2O molecules, whereas, in engelhauptite, extra-framework positions are occupied by K^+ and Cl^- ions. By analogy with volborthite, the idealized formula of engelhauptite can be written as $\text{Cu}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \text{KCl}$. Structural similarity between the two minerals is manifested by the closeness of their reduced unit-cell volumes equal to 441 Å³ for engelhauptite and 449 Å³ for volborthite. The two minerals crystallize in different crystal systems, but the *a* unit-cell parameter of engelhauptite is close to the *b* parameter of volborthite, whereas the *c* parameter of engelhauptite is close to the doubled *c* parameter of volborthite (Table 5). The relations between the *a* parameters of the two minerals can be described as $a_{\text{volb}} \sim 3^{1/2} a_{\text{eng}}$ (note that the unit cell of volborthite is *I*-centered (Kashaev et al. 2008)). The unusual [2+4] distortion of an octahedral coordination geometry in volborthite was first reported by Basso et al. (1988) (see also: Lafontaine et al. 1990) for the refinement in the space group *C2/m*, which prompted Burns and Hawthorne (1996) to consider this mineral as a possible example of dynamic disorder of the Jahn-Teller octahedral geometry. However, Kashaev et al. (2008) refined the crystal structure of volborthite in the space group *Ia* and

demonstrated that the reduction of symmetry results in all Cu sites possessing typical [4+2]-distorted octahedral geometries. The [2+4] distortion observed in the *C2/m* model of volborthite is thus an overlap of two [4+2]-distorted geometries in different orientations. It is very likely that the [2+4] geometry found

Table 5 Comparative data for engelhauptite and volborthite

Mineral	Engelhauptite	Volborthite
Formula	$\text{KCu}_3(\text{V}_2\text{O}_7)(\text{OH})_2\text{Cl}$	$\text{Cu}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$
Crystal system	Hexagonal	Monoclinic
Space group	<i>P6₃/mmc</i>	<i>Ia</i> ^a
<i>a</i> , Å	5.922	10.646
<i>b</i> , Å		5.867
<i>c</i> , Å	14.513	14.432
β , °		95.19
<i>V</i> , Å ³	441	898
<i>Z</i>	2	2
<i>D</i> , g cm ⁻³	3.86 (calc.)	3.5–3.8
Strongest reflections of the X-ray powder pattern (<i>d</i> , Å – <i>I</i>)	7.32–98 4.224–17 2.979–100 2.759–19 2.565–18 2.424–18 1.765–16	7.166–100 2.999–30 2.639–25 2.560–55 2.551–30 2.381–50
Colour	Yellow brown to brown	Green to dark olive green
Optical data	Uniaxial (+) $\omega=1.978$ $\varepsilon=2.021$	Biaxial (+) or (–) $\alpha=1.820\text{--}2.01$ $\beta=1.835\text{--}2.05$ $\gamma=1.92\text{--}2.07$ $2 V(\text{meas})=63\text{--}83^\circ$
References	This work	Basso et al. (1988); Matsubara et al. (1990); Kashaev et al. (2008)

^a crystallographic data according to Kashaev et al. (2008)

for the Cu site in engelhauptite is also an artefact of the average structure model obtained in the course of X-ray diffraction structure analysis. It may well be suggested that the studies of crystals of engelhauptite of better quality will reveal similar overlaps of [4+2] coordinations as observed in volborthite.

Both engelhauptite and volborthite are also structurally related to martyite, $\text{Zn}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (Kampf and Steele 2008), which is trigonal, $P\bar{3}m1$, $a=6.0818(4)$, $c=7.1793(10)$ Å and $V=229.97(4)$ Å³. It can easily be seen that the unit cell of martyite is approximately half of that of engelhauptite.

Engelhauptite is a hydroxyl-bearing mineral, which at the same time contains K and Cl, similarly to the fumarolic copper vanadates. It occurs in the mineral assemblage related to young volcanic rocks and may form from the low-temperature hydrothermal solutions at the last stage of a post-eruption activity. Alternatively, it may be a product of a supergene alteration of primary copper sulfides. We consider the supergene origin as most probable, taking into account typical supergene minerals occurring either together with engelhauptite (volborthite, allophane) or in neighbouring cavities (malachite, tangeite, chrysocolla). The presence of OH groups in the new mineral could be an important argument for its supergene origin, taking into account general genetic features of natural copper vanadates (see Introduction). Chalcopyrite reported for the volcanic rocks of Kahlenberg (Blass and Schüller 2011) could be a source of copper, whereas vanadium is a typical minor constituent of the Eifel basalts. Another possible source of V is primary anhydrous fumarolic vanadates. The intimate association of such chemically and structurally similar minerals as engelhauptite and volborthite (Fig. 1a) may indicate their common origin from low-temperature solutions, when engelhauptite plays the role of a sink for both K^+ and Cl^- ions.

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References

- Anthony JW, Bideaux RA, Bladh KW, Nichols MC (2000) Handbook of mineralogy. Vol. IV. Arsenates, Phosphates, Vanadates. Mineral Data Publishing, Tucson
- Basso R, Palenzona A, Zefiro L (1988) Crystal structure refinement of volborthite from Scrava Mine (Eastern Liguria, Italy). *N Jb Miner Mh* 385–394
- Blass G, Schüller W (2011) “Unglaubliche” Kupferminerale aus der Vulkaneifel: Auf’m Kopp bei Neroth. *Lapis* 36:21–28, 90
- Burns PC, Hawthorne FC (1996) Static and dynamic Jahn-Teller effects in Cu^{2+} oxysalt minerals. *Can Mineral* 34:1089–1105
- Kampf AR, Steele IM (2008) Martyite, a new mineral species related to volborthite: description and crystal structure. *Can Mineral* 46:687–692
- Kashaev AA, Rozhdensvenskaya IV, Bannova II, Sapozhnikov AN, Glebova OD (2008) Balance, uniformity and asymmetry of the structure of volborthite $\text{Cu}_3(\text{OH})_2(\text{V}_2\text{O}_7) \cdot 2(\text{H}_2\text{O})$. *J Struct Chem* 49:708–711
- Lafontaine MA, Le Bail A, Ferey G (1990) Copper-containing minerals - I. $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2(\text{H}_2\text{O})$: the synthetic homolog of volborthite; crystal structure determination from X-ray and neutron data; structural correlations. *J Solid State Chem* 85:220–227
- Leu K (1995) Der vulkanabbau “Auf’m Kopp” bei Oberstadtfeld in der Westeifel. *Lapis* 2:17–20
- Libowitzky E (1999) Correlation of O–H stretching frequencies and O–H···O hydrogen bond lengths in minerals. *Monatsh Chem* 130: 1047–1059
- Matsubara S, Saito Y, Kato A (1990) Vanadium minerals in siliceous sedimentary rocks from Unuma, Gifu Prefecture, Japan, with special reference to volborthite and roscoelite. *J Mineral Petrol Econ Geol* 85:522–530
- Pekov IV, Zelenski ME, Yapaskurt VO, Polekhovsky YS, Murashko MN (2013a) Starovaite, $\text{KCu}_5\text{O}(\text{VO}_4)_3$, a new mineral from fumarole sublimates of the Tolbachik volcano, Kamchatka, Russia. *Eur J Mineral* 25:91–96
- Pekov IV, Zubkova NV, Zelenski ME, Yapaskurt VO, Polekhovsky YS, Fadeeva OA, Pushcharovsky DY (2013b) Yaroshevskite, $\text{Cu}_9\text{O}_2(\text{VO}_4)_4\text{Cl}_2$, a new mineral from the Tolbachik volcano, Kamchatka, Russia. *Mineral Mag* 77:107–116
- Pekov IV, Zubkova NV, Yapaskurt VO, Kartashov PM, Polekhovsky YS, Murashko MN, Pushcharovsky DY (2014) Koksharovite, $\text{CaMg}_2\text{Fe}^{3+}_4(\text{VO}_4)_6$, and grigorievite, $\text{Cu}_3\text{Fe}^{3+}_2\text{Al}_2(\text{VO}_4)_6$, two new howarddevansite-group minerals from volcanic exhalations. *Eur J Mineral* 26:667–677
- Sheldrick GM (2008) A short history of SHELX. *Acta Crystallogr A* 64: 112–122
- Sokolova EV, Hawthorne FC, Karpenko VY, Agakhanov AA, Pautov LA (2004) Turanite, $\text{Cu}^{2+}_5(\text{V}^{5+}\text{O}_4)_2(\text{OH})_4$, from the Tyuya-Muyun radium-uranium deposit, Osh District, Kyrgyzstan: a new structure for an old mineral. *Can Mineral* 42:731–739
- WinX^{Pow} Software (2002) STOE and CIE GmbH
- Zelenski ME, Zubkova NV, Pekov IV, Boldyreva MM, Pushcharovsky DY, Nekrasov AN (2011) Pseudolyonsite, $\text{Cu}_3(\text{VO}_4)_2$, a new mineral species from the Tolbachik volcano, Kamchatka Peninsula, Russia. *Eur J Mineral* 23:475–481