

Klajite, $\text{MnCu}_4(\text{AsO}_4)_2(\text{AsO}_3\text{OH})_2(\text{H}_2\text{O})_{10}$, from Jáchymov (Czech Republic): the second world occurrence

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ABSTRACT

Klajite, $\text{MnCu}_4(\text{AsO}_4)_2(\text{AsO}_3\text{OH})_2(\text{H}_2\text{O})_{10}$, the Mn-Cu-bearing member of the lindackerite group, was found in Jáchymov, Czech Republic, as the second world occurrence. It is associated with ondrúšite and other arsenate minerals growing on the quartz gangue with disseminated primary sulfides, namely tennantite and chalcopyrite. Electron-microprobe data showed klajite aggregates to be chemically inhomogeneous at larger scales, varying from Mn-Ca-rich to Cu-rich domains. The chemical composition of the Mn-rich parts of aggregates can be expressed by the empirical formula $(\text{Mn}_{0.46}\text{Ca}_{0.22}\text{Cu}_{0.07}\text{Mg}_{0.02})_{\Sigma 0.77}(\text{Cu}_{3.82}\text{Mg}_{0.14}\text{Ca}_{0.03}\text{Zn}_{0.01})_{\Sigma 4.00}(\text{As}_{1.94}\text{Si}_{0.06})_{\Sigma 2.00}\text{O}_8[\text{AsO}_{2.73}(\text{OH})_{1.27}]_2(\text{H}_2\text{O})_{10}$ (mean of seven representative spots; calculated on the basis of As + Si + P = 4 a.p.f.u. (atoms per formula unit) and 10 H_2O from ideal stoichiometry), showing a slight cationic deficiency at the key *Me*-site. According to single-crystal X-ray diffraction, klajite from Jáchymov is triclinic, $P\bar{1}$, with $a = 6.4298(8)$, $b = 7.9716(8)$, $c = 10.707(2)$ Å, $\alpha = 85.737(12)^\circ$, $\beta = 80.994(13)^\circ$, $\gamma = 84.982(10)^\circ$, and $V = 538.85(14)$ Å³, $Z = 1$. The crystal structure was refined to $R_1 = 0.0628$ for 1034 unique observed reflections (with $I_{\text{obs}} > 3\sigma(I)$), confirming that klajite (Mn-Cu member) and ondrúšite (Ca-Cu member) are isostructural. The current data-set allowed determination of the positions of several hydrogen atoms. Discussion on hydrogen bonding networks in the structure of klajite as well as detailed bond-valence analysis are provided.

KEYWORDS: klajite, oxide zone, lindackerite group, arsenate hydrate, crystal structure, bond valence, Jáchymov.

Introduction

KLAJITE was described originally by Szakáll *et al.* (2011) from Recsk in Hungary, as a new member of the lindackerite group of minerals. The name-bearing member of the group, lindackerite, was described in 1853 by Josef Florian Vogl from the Geister vein in Jáchymov, Bohemia (Vogl, 1853). Since that time seven additional members of the

group have been discovered: chudobaite (Strunz, 1960), geigerite (Greaser *et al.*, 1989), pradetite (Sarp and Dominik, 1995; Burke *et al.*, 2007), veselovskýite (Sejkora *et al.*, 2010), ondrúšite (Sejkora *et al.*, 2011) and hloušekite (Plášil *et al.*, 2013). The general chemical composition of the lindackerite-like mineral can be expressed by the formula $\text{Me}^{2+}\text{M2M3}(\text{AsO}_4)_2(\text{AsO}_3\text{OH})_2 \cdot 9\text{--}10\text{H}_2\text{O}$, $Z = 1$, where the *Me* position is occupied by a divalent cation (e.g. Mn, Ca, Co, Ni, Zn or Cu) and the M2 and M3 sites are usually occupied by Cu, but can be also occupied by Zn or Mg.

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Here we present new structure data for klajite with a redefined content of molecular H₂O in the structure. Along with the new, more accurate structure data for the Mn/Ca-bearing members of the lindackerite group we present the results of microprobe analysis documenting the elemental variability at the cationic sites in these minerals.

Occurrence

The klajite studied here was identified on specimen #1225K from the systematic collection of mineral species of one of the authors (AVK). It was collected by Czech mineral collector B. Bureš in the early 2000s at the vein Sv. Trojice ('Dreifaltigkeit gang' in German), Svornost Mine, Jáchymov, Western Bohemia, Czech Republic, the type locality for ondrůšite (Sejkora *et al.*, 2011). The studied sample represents a 6 cm × 4 cm × 2 cm piece of quartz-gangue with disseminated altered primary sulfides (namely tennantite and chalcopyrite). Secondary minerals growing on the surface include ondrůšite, geminite, lavendulan, picropharmacolite and köttigite. Our attention was drawn to the yellow-green transparent crystalline aggregates lying on the blue lavendulan and geminite and clearly differing by its colour from pale-greenish ondrůšite. These aggregates were subsequently identified as klajite (Fig. 1). To the best of our knowledge, Jáchymov thus represents the second world occurrence of this extremely rare mineral after its type locality in Lejtakna, Reck, Mátra Mts., Hungary (Szakáll *et al.*, 2011).

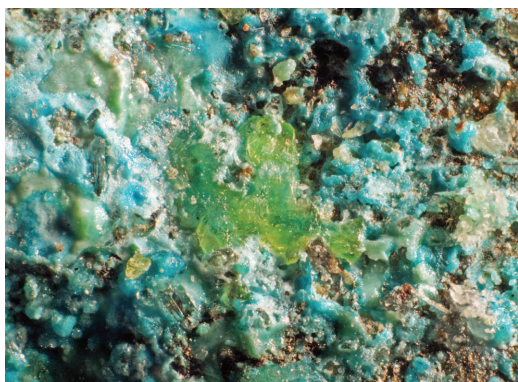


FIG. 1. Klajite from Jáchymov: yellowish-green crystals growing on altered surface of quartz-gangue along with lavendulan (bluish) and ondrůšite (on the right, pale greenish). FOV: 3.0 mm. Photo: P. Škacha.

Chemical composition

The chemical composition of the klajite aggregate was determined using a Cameca SX100 electron microprobe (WDS mode, 15 kV, 10 nA and 10 µm beam diameter) from five point analyses (analyst R. Škoda). The following X-ray lines and standards were selected: K α lines: almandine (Fe), fluorapatite (Ca, P), sanidine (Al, K), albite (Na), synthetic Mg₂SiO₄ (Mg), spessartine (Mn, Si), synthetic ScVO₄ (V), topaz (F), vanadinite (Cl), synthetic SrSO₄ (S), lammerite (Cu); L α lines: lammerite (As). Peak counting times (CT) were 10–20 s and the counting time for background was 50% of the peak CT. The measured intensities were converted to element concentrations using the PAP matrix correction program (Pouchou and Pichoir, 1985). The difference between acquired analytical totals and theoretical 100 wt.% is considered to be caused by water and this amount of water was involved in the matrix correction.

According to the electron microprobe study of the fragment containing 'lindackerites' (Fig. 2), the chemical composition of this large fragment is quite inhomogeneous (Table 1), with two dominant mineral components: more dominant klajite and less dominant ondrůšite (Fig. 3). According to the microprobe data, there are two principal substitution trends: CuMn (corresponding to lindackerite–klajite solid solution) and CaMn (corresponding to ondrůšite–klajite solid solution).

The empirical formula of the Mn-dominant part of the sample studied, corresponding to klajite, is:

$$(\text{Mn}_{0.46}\text{Ca}_{0.22}\text{Cu}_{0.07}\text{Mg}_{0.02})_{\Sigma 0.77}(\text{Cu}_{3.82}\text{Mg}_{0.14}\text{Ca}_{0.03}\text{Zn}_{0.01})_{\Sigma 4.00}(\text{As}_{1.94}\text{Si}_{0.06})_{\Sigma 2.00}\text{O}_8[\text{AsO}_{2.73}(\text{OH})_{1.27}]_2(\text{H}_2\text{O})_{10} \text{ (mean of seven representative spots; calculated on the basis of As + Si + P = 4 a.p.f.u. and 10 H}_2\text{O from ideal stoichiometry)}.$$

The empirical formula of the Cu-dominant part of the sample studied, corresponding to lindackerite, is: $(\text{Cu}_{0.62}\text{Mn}_{0.14}\text{Ca}_{0.01})_{\Sigma 0.77}(\text{Cu}_{3.97}\text{Mg}_{0.03}\text{Fe}_{0.01})_{\Sigma 4.01}(\text{As}_{1.97}\text{Si}_{0.03})_{\Sigma 2.00}\text{O}_8[\text{AsO}_{2.77}(\text{OH})_{1.23}]_2(\text{H}_2\text{O})_{10}$ (mean of five representative spots; calculated on the base of As + Si = 4 a.p.f.u. and 10 H₂O from ideal stoichiometry).

Single-crystal X-ray diffraction

A tabular yellowish crystal of klajite, of dimensions 0.239 mm × 0.123 mm × 0.094 mm, was selected under the optical microscope based on its optical properties and used for diffraction

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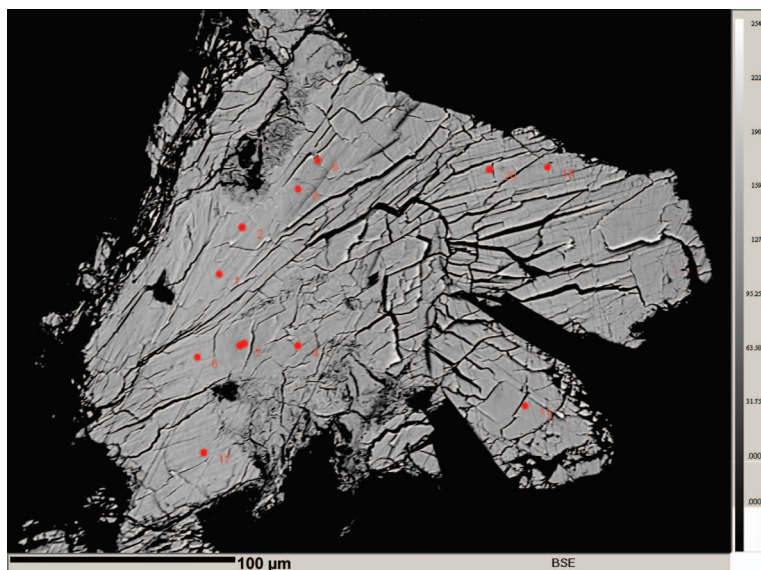


FIG. 2. Klajite in polished section used for electron microprobe study. The spot analyses are represented by the red dots. BSE image (Cameca SX100).

experiments on an Oxford Diffraction Gemini single-crystal four-circle diffractometer.

Graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) from the conventional sealed X-ray

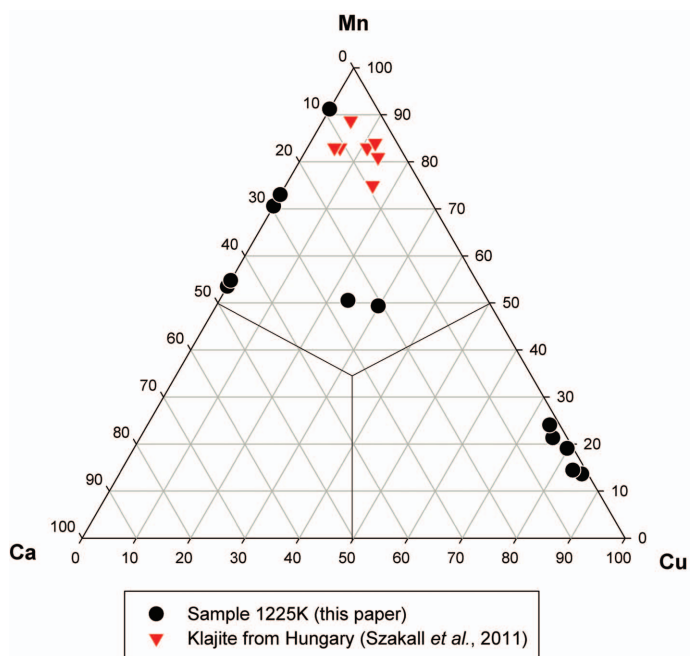


FIG. 3. Ternary plot of the cation contents at the *Me* site for klajite (Mn)–lindackerite (Cu)–ondrušite (Ca) series of the lindackerite group.

TABLE 1. Chemical composition of lindackerite-like minerals studied.

Wt. %	Klajite			Lindackerite		
	Mean (<i>n</i> = 7)	Range	St. dev.	Mean (<i>n</i> = 5)	Range	St. dev.
MgO	0.65	0.46–0.72	0.10	0.10	0.03–0.28	0.05
CaO	1.35	0.88–1.81	0.34	0.09	0.08–0.13	0.02
MnO	3.18	2.62–4.35	0.31	0.95	0.80–1.13	0.12
FeO	b.d.l.	–	–	0.04	0.02–0.07	0.02
CuO	30.24	29.64–31.71	0.68	35.19	34.03–35.91	0.76
ZnO	0.05	0.05–0.30	0.11	b.d.l.	–	–
SiO ₂	0.32	0.22–0.40	0.07	0.16	0.12–0.23	0.05
P ₂ O ₅	0.04	0.02–0.19	0.07	b.d.l.	–	–
As ₂ O ₅	44.30	43.76–44.41	0.23	43.96	43.68–44.57	0.34
H ₂ O*	19.87			19.51		
Total	100.00			100.00		
Mg	0.16			0.03		
Ca	0.25			0.01		
Mn	0.46			0.14		
Fe				0.01		
Cu	3.89			4.59		
Zn	0.01					
Si	0.06			0.03		
P	0.01					
As	3.94			3.97		
OH	1.27			1.23		

a.p.f.u. coefficients calculated on the basis of (As + Si + P) = 4 a.p.f.u. and 10 H₂O from ideal stoichiometry.

* H₂O calculated on the basis of the content of 10 H₂O from ideal stoichiometry plus charge balance.

b.d.l.: below detection limit

tube, collimated by a fibre optics Mo-Enhance collimator and detected by an Atlas CCD detector, was used for the diffraction experiments. Single-crystal data showed that klajite is triclinic, $P\bar{1}$, with $a = 6.4298(8)$, $b = 7.9716(8)$, $c = 10.707(2)$ Å, $\alpha = 85.737(12)^\circ$, $\beta = 80.994(13)^\circ$, $\gamma = 84.982(10)^\circ$ and $V = 538.85(14)$ Å³. A total of 2620 reflections was measured; of these, 1918 were unique and 1036 were classified as observed, with the criterion [$I_{\text{obs}} > 3\sigma(I)$]. Intensity data were corrected for Lorentz effect, polarization and background, and a combined absorption correction (multi-scan and analytical correction based on the method of Clark and Reid, 1995) was applied (*CrysAlis RED*; Agilent Technologies, 2012), leading to R_{int} of 0.0413. The experimental conditions are given in Table 2.

The charge-flipping algorithm (Oszlányi and Sütő, 2004, 2008; Palatinus, 2013), implemented in the Superflip program (Palatinus and Chapuis, 2007), was used for the structure solution. The model obtained was refined subsequently using

the full-matrix least-squares algorithm (based on F^2) of the *Jana2006* program-suite (Petříček *et al.*, 2006). The solution obtained from the *Superflip* program confirmed the chosen space group $P\bar{1}$. Nearly, all atoms were found by the structure solution, except those O atoms that belong to the H₂O ligands coordinated to the Mn²⁺ cation. These O atoms were localized from the difference-Fourier maps. Hydrogen atoms were not localized from the current diffraction data with respect to their resolution. All atoms were refined with anisotropic displacement parameters (ADP) (excluding O12 atom, which produced physically unrealistic values). Refinement including 155 parameters converged to the final $R_1 = 0.0628$ for 1034 unique observed reflections (Table 2). The final atom coordinates and the displacement parameters are given in Table 3. The selected interatomic distances are listed in Tables 4 and 5. The results of the bond-valence analysis, following the procedure of Brown (1981, 2002) are given in Table 6.

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TABLE 2. Summary of data collection conditions and refinement parameters for klajite.

Ideal structural formula	Mn _{0.808} Cu ₄ (AsO ₄) ₂ (AsO ₃ OH) ₂ (H ₂ O) ₁₀
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.4298(8), 7.9716(9), 10.707(2)
α , β , γ (°)	85.737(12), 80.944(13), 84.982(10)
<i>V</i> (Å ³)	538.85(14)
Space group	<i>P</i> $\bar{1}$
<i>Z</i>	1
<i>D</i> _{calc.} (g.cm ⁻³)	3.140
Temperature (K)	300
Wavelength (Å)	MoK α , 0.71073
Crystal dimensions (mm)	0.239 × 0.123 × 0.094
Collection mode, frame width, count time	ω scans, 1.0°, 80 s
Limiting θ angles (°)	3.10–25.90
Limiting Miller indices	$-7 \leq h \leq 6$, $-7 \leq k \leq 9$, $-13 \leq l \leq 12$
No. of reflections measured	2607
No. of unique reflections	1916
No. of observed reflections (criterion)	1034 [<i>I</i> _{obs} > 3 σ (<i>I</i>)]
Completeness to θ max., <i>R</i> _{int}	0.81, 0.0413
Absorption correction (mm ⁻¹), <i>T</i> _{min} / <i>T</i> _{max}	10.6, 0.234/0.440
<i>F</i> ₀₀₀	483
Refinement by Jana2006 on <i>F</i>²	
Parameters refined, restraints, constraints	150, 4, 9
<i>R</i> ₁ , <i>wR</i> ₂ (obs)	0.0628, 0.1167
<i>R</i> ₁ , <i>wR</i> ₂ (all)	0.1249, 0.1426
GOF obs/all	1.53/1.34
$\Delta\rho_{\min}$, $\Delta\rho_{\max}$ (e/Å ³)	−1.61, 1.88
Weighting scheme, weights	σ , <i>w</i> = 1/($\sigma^2(F)$ + 0.0004 <i>F</i> ²)

Crystal structure of klajite

The general structural architecture of klajite is similar to the other members of the lindackerite group of minerals (Fig. 4). For details we refer to the papers by Hybler *et al.* (2003) and Sejkora *et al.* (2011), who provided the description of ondrušíte, the Ca²⁺-bearing lindackerite. From the current structure study, klajite was found to be isostructural with ondrušíte. The details of the interstitial settings in klajite and a sketch for a hydrogen-bonding system in klajite and ondrušíte are presented below.

Interstitial bonds

Based on the current data set, it was not possible to find the positions of all the hydrogen atoms from the difference Fourier maps. However, some assumptions can be made, based on the refined positions of the hydrogen atom of the AsO₃OH group, the localized hydrogen atoms of the H₂O molecule (O9) and the bonding matrix obtained from the bond-valence analysis (Table 6).

There are two independent O sites (O4 and O10), coordinated to the *Me* site occupied by Mn²⁺, identified by the bond-valence analysis (Table 5) as belonging to the H₂O molecules. Two independent O sites (O5 and O7), also identified as H₂O molecules, are localized within the sheets and belong to the CuΦ₆ (Φ is an unspecified ligand atom) polyhedra. There is an isolated O site in the interlayer (O9) which is held in the structure by hydrogen bonding only. The O3 atom was found by bond-valence analysis to be the most undersaturated, at 1.20 vu, and thus belonging to a protonated O atom of the acid hydrogen arsenate group [AsO₃(OH)]^{2−}.

Based on the bond-valence analysis (Table 5, schematic in Fig. 5) we propose the following scheme for a hydrogen-bond network in the structure of klajite. The H-bond emanating from the protonated As1 tetrahedron (H1) is accepted by the O9 atom, which belongs to the uncoordinated H₂O group (at the distance of 2.95 Å). The two H bonds emanating from this interstitial H₂O group, not bonded directly to any cation, are received at both sides of adjacent sheets by O2

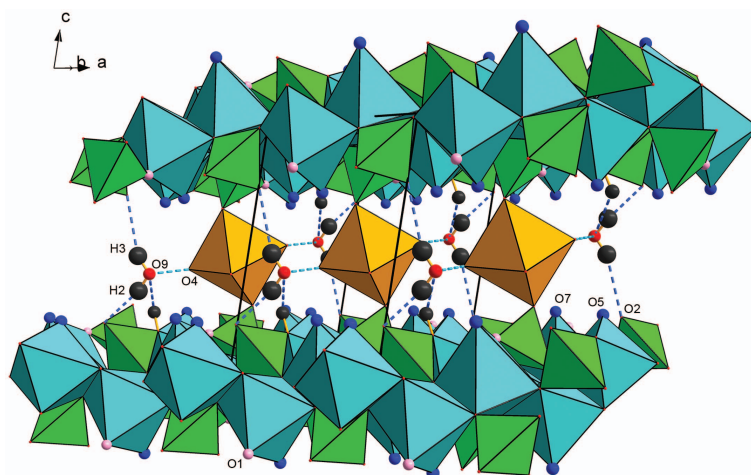


FIG. 4. Crystal structure of klajite. $\text{Cu}\Phi_6$ polyhedra (azure) and As-tetrahedra (green) share vertices and edges to form the sheets; adjacent sheets are linked via Mn octahedra (orange). The interstitial linkage is supported by a complicated network of hydrogen bonds involving a single H_2O group not bonded directly to any cation ($\text{H2}-\text{O9}-\text{H3}$), H_2O groups coordinated to Mn^{2+} (O4, O10), H_2O groups coordinated to the Cu^{2+} (atoms in blue; O5, O7) and O sites with bond-valence deficiency (O2 of the As tetrahedra; O1 in purple). The proposed H bond between O4 and O9 is displayed in light blue; other proposed H bonds were omitted for clarity.

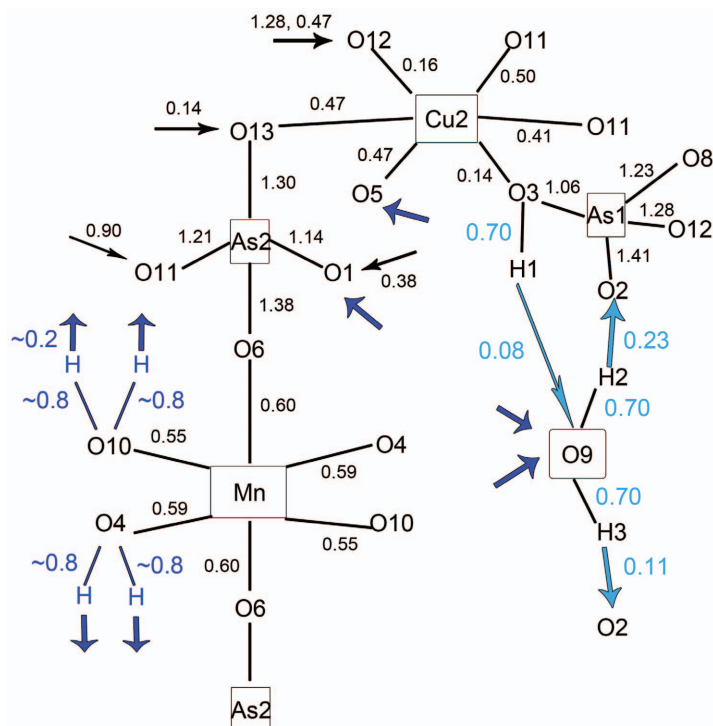


FIG. 5. General schematic showing bond-valence values (in vu) associated with the current bonds obtained from the refinement and proposed H-bond network in the klajite structure. Light blue corresponds to the refined H-atom parameters, dark blue arrows indicate contributions of the proposed H bonds (of ~ 0.2 vu) to the bonding network.

TABLE 3. Atom coordinates and displacement parameters ($U_{\text{iso}}/U_{\text{eq}}$, in $\text{\AA}^2$) for klajite.

	x/a	y/b	z/c	$U_{\text{iso}}/U_{\text{eq}}$	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.0867(2)	0.11813(18)	0.12977(18)	0.0211(6)	0.0102(8)	0.0094(8)	0.0449(13)	-0.0009(6)	-0.0060(8)	-0.0063(8)
As2	-0.4163(2)	0.51739(18)	0.16079(17)	0.0204(6)	0.0090(8)	0.0116(9)	0.0417(13)	-0.0004(6)	-0.0057(8)	-0.0049(8)
Cu1	-0.3893(3)	0.1325(2)	0.0604(2)	0.0227(7)	0.0100(10)	0.0135(10)	0.0460(15)	-0.0011(7)	-0.0045(10)	-0.0104(9)
Cu2	0.1057(3)	0.5741(2)	0.0952(2)	0.0228(7)	0.0114(10)	0.0138(11)	0.0449(15)	-0.0015(7)	-0.0071(10)	-0.0058(9)
Mn [#]	-0.5	0.5	0.5	0.0296(19)	0.020(3)	0.021(3)	0.047(4)	-0.0019(18)	0.001(2)	-0.004(2)
O1	-0.4677(14)	0.3092(12)	0.1914(10)	0.023(3)*						
O2	0.0051(14)	-0.0168(12)	0.2466(11)	0.030(4)	0.016(6)	0.017(6)	0.061(9)	-0.006(4)	-0.012(6)	-0.013(6)
O3	0.1354(15)	0.2972(12)	0.2014(11)	0.028(4)	0.023(6)	0.017(6)	0.041(8)	0.004(5)	-0.002(6)	-0.004(6)
O4	-0.7933(17)	0.4026(14)	0.4529(12)	0.042(5)	0.037(7)	0.049(8)	0.045(9)	-0.004(6)	-0.018(6)	-0.012(7)
O5	0.0156(14)	0.6539(11)	0.2656(11)	0.030(4)	0.009(5)	0.017(6)	0.064(9)	0.001(4)	-0.006(6)	-0.011(6)
O6	-0.3974(15)	0.5890(12)	0.2986(10)	0.026(4)	0.028(6)	0.019(6)	0.030(8)	-0.001(5)	-0.002(6)	-0.009(5)
O7	0.5838(16)	0.9527(12)	0.2658(11)	0.030(4)	0.038(7)	0.022(6)	0.034(8)	-0.002(5)	-0.018(6)	-0.008(5)
O8	0.3250(13)	0.0625(11)	0.0463(10)	0.018(4)	0.010(5)	0.016(6)	0.030(7)	0.001(4)	-0.007(5)	-0.007(5)
O9	0.2375(4)	0.0475(11)	0.4383(10)	0.052(5)	0.052(8)	0.049(8)	0.053(10)	-0.018(6)	-0.006(7)	0.019(7)
O10	-0.3227(17)	0.2571(14)	0.4322(13)	0.054(6)	0.044(8)	0.035(8)	0.082(12)	0.005(6)	-0.015(8)	-0.001(7)
O11	-0.1860(13)	0.5390(11)	0.0612(9)	0.016(2)*						
O12	-0.0881(14)	0.1711(11)	0.0300(9)	0.019(2)*						
O13	-0.6044(14)	0.6314(11)	0.0939(10)	0.022(3)*						
H1	0.06(2)	0.321(17)	0.277(7)	0.0333*						
H2	0.1646(9)	0.055(2)	0.3715(9)	0.062*						
H3	0.1493(8)	0.023(5)	0.5106 (7)	0.062*						

[#] The refined occupancy for the Mn site is 0.808(11). Atoms marked with * were refined with isotropic displacement parameters.

TABLE 4. Selected interatomic distances (in Å) for klajite.

Cu1–O1	2.038(10)	Cu2–O3	2.414(10)
Cu1–O7 ⁱⁱ	2.526(11)	Cu2–O5	1.960(12)
Cu1–O8 ⁱⁱⁱ	1.997(9)	Cu2–O11	2.012(9)
Cu1–O8 ⁱ	1.973(10)	Cu2–O11 ^v	1.938(10)
Cu1–O12	1.961(9)	Cu2–O12 ^v	2.353(9)
Cu1–O13 ^{iv}	2.412(10)	Cu2–O13 ^{vi}	1.955(10)
<Cu1–O>	2.15	<Cu2–O>	2.11
As1–O2	1.640(10)	As2–O1	1.718(9)
As1–O3	1.744(11)	As2–O6	1.647(11)
As1–O8	1.689(8)	As2–O11	1.697(8)
As1–O12	1.677(10)	As2–O13	1.669(10)
<As1–O>	1.69	<As2–O>	1.68
Mn–O4	2.242(12)		
Mn–O4 ^{vii}	2.242(12)		
Mn–O6	2.236(10)		
Mn–O6 ^{vii}	2.236(10)		
Mn–O10	2.267(11)		
Mn–O10 ^{vii}	2.267(11)		
<Mn–O>	2.25		
O1–O3 ⁱⁱⁱ	2.547(14)	O5–O6	2.713(13)
O1–O6	2.687(15)	O5–O11	2.950(16)
O1–O7 ⁱⁱ	2.899(13)	O5–O13 ^{vi}	2.817(13)
O1–O10	2.868(18)	O6–O7 ⁱⁱⁱ	2.888(13)
O1–O11	2.826(13)	O6–O10	2.952(15)
O1–O12	2.940(12)	O6–O11	2.726(14)
O1–O13	2.820(13)	O6–O13	2.723(15)
O2–O3	2.695(14)	O7–O9 ^x	2.750(12)
O2–O5 ^{viii}	2.614(13)	O8–O8 ^{xi}	2.469(12)
O2–O7 ⁱⁱ	2.715(14)	O8–O12	2.748(12)
O2–O8	2.805(13)	O8–O12 ⁱ	2.751(14)
O2–O9	2.822(15)	O9–O10 ^{ix}	2.761(14)
O2–O12	2.783(15)	O11–O11 ^v	2.589(12)
O3–O4 ^{vi}	2.993(18)	O11–O12	2.978(12)
O3–O5	2.981(14)	O11–O13	2.701(12)
O3–O8	2.678(14)	O11–O13 ^{iv}	2.789(15)
O3–O11 ^v	2.993(14)	O12–O12 ⁱ	2.937(12)
O3–O12	2.793(16)	O12–O13 ^{iv}	2.849(13)
O4–O9 ⁱⁱⁱ	2.835(14)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $x-1, y-1, z$; (iii) $x-1, y, z$; (iv) $-x-1, -y+1, -z$; (v) $-x, -y+1, -z$; (vi) $x+1, y, z$; (vii) $-x-1, -y+1, -z+1$; (viii) $x, y-1, z$; (ix) $-x, -y, -z+1$; (x) $x, y+1, z$; (xi) $-x+1, -y, -z$.

TABLE 5. Hydrogen-bond geometry (in Å, °) for the structure of klajite.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$\angle D-H\cdots A$
O3–H1 $\cdots$ O9	0.91(9)	2.95(12)	3.221(14)	99(9)
O9–H2 $\cdots$ O2	0.911(13)	1.954(16)	2.822(15)	158.6(19)
O9–H3 $\cdots$ O2	0.904(13)	2.631(13)	3.487(14)	158(2)

atoms (at distances 1.95 and 2.63 Å; contributing ~0.3 vu to O2). Moreover, this H₂O group can still accept two additional weaker hydrogen bonds to satisfy fully the bond-valence requirements. Thus it is an inverse transformer H₂O group, most probably where the O atom is [5]-coordinated (Fig. 5). We noticed that O3–H1–O9 is somewhat strained in the proposed scheme, with <O3–H1–O9> close to 100°; however we are convinced that it might be an artifact of the weak dataset. The hydrogen atoms of the H₂O groups coordinated to the Mn²⁺ cation were not localized; however, based on the bond-valence scheme and considerations stated above, we conclude that the bond-valence requirements of each of these O atoms are perfectly satisfied by the linking of two hydrogen atoms (each of which provides ~0.80 vu) (Fig. 5). The hydrogen bonds emanating from these O4 and O10 atoms are received either by the interstitial H₂O group (O9 atom) or undersaturated O atoms within the structure unit, which still might accept incident bond-valence (O1, O2). The O5 atom, which is coordinated by the Cu2 polyhedra, was also identified as the H₂O group (Table 6). Its bond-valence should be perfectly satisfied by bonding to two H atoms (each of them contributing ~0.8 vu). The O7 atom was identified as the second H₂O group on the sheet. Besides the linkage to Cu1 (~0.1 vu) and to the two H atoms (each contributing ~0.8 vu), this atom is able to accept additional bond valence, e.g. hydrogen bond (~0.2 vu). Based on the previously given sums, we can conclude that the H bonds emanating from the O5 can be received by the O7 and the bonds from O7 probably emanate towards the interlayer, where they can be accepted by O9. Finally, the O5 atom is probably a transformer group, where the O atom is [3]-coordinated, as are the O4 and O10 atoms. The remaining H₂O group, the O7 atom, can be a non-transformer or also an inverse-transformer group.

Structural formula

Based on the results of the structure refinement and bond-valence analysis, the formula of klajite is Mn_{0.81}Cu₄(AsO₄)₂(AsO₃OH)₂(H₂O)₁₀, *Z* = 1. The question regarding the reduced occupancy of the Mn site is whether it is just an artefact of the data (split crystal, absorption effects), or if it reflects mixing of the lighter and heavier elements at the site (see results of the electron microprobe

study). Attempts to treat the Mn site as a mixed site (including Ca²⁺ and Mg²⁺) were unsuccessful as it was unstable. We decided to present the data with the refined site occupancy of the Mn site, as it is followed by a decrease in the *R*₁ factor of ~0.5%, thus leading to a better fit to the data.

Discussion and conclusions

Relationship of klajite and ondrúšite

We have described the crystal structure of klajite, which is closely related to the structure of ondrúšite, CaCu₄(AsO₄)₂(AsO₃OH)₂(H₂O)₁₀, described from Jáchymov by Sejkora *et al.* (2011). We conclude that those two minerals are isostructural, based on the results of the structure refinement. Moreover, we conclude, based on the microprobe study, that the Mn–Ca substitution should exist, at least to some extent. Interestingly, no Mn²⁺ was found by the microprobe study of ondrúšite (Sejkora *et al.*, 2011), even if the sample originated from the same locality (the vein of Sv. Trojice). The current single-crystal XRD experiment provided better data, which is reflected by better results of the structure refinement, compared to the ondrúšite study (Sejkora *et al.*, 2011). We conclude that klajite should contain 10 instead of 9 molecules of H₂O as was given in the original description of klajite by Szakáll *et al.* (2011).

Relationship to the lindackerite group of minerals

Klajite is thus the Mn-bearing member of the klajite–ondrúšite–geigerite–chudobaite series of the lindackerite group of minerals. The crystal structures of the lindackerite–pradetite–veselovskýite–hloušekite (IMA 2013-048; Plášil *et al.*, 2013) series of the group differ from that, investigated here. The main differences are in the coordination-pathway of the *Me* in the interlayer. In the klajite structure (and also, for example in ondrúšite), the divalent cation is coordinated by six ligand atoms as a more or less distorted octahedron. In the lindackerite structure (Hybler *et al.*, 2003) divalent metals are coordinated by the eight ligand O atoms in the horizontal plane of the octahedron. Those O sites have 50% occupancy; thus they represent a projection of the two different *Me*²⁺ octahedra. The unit-cell volume of those phases reflects the size of the interlayer cation and the manner of coordination. For the klajite–ondrúšite–geigerite–chudobaite

TABLE 6. Bond-valence analysis for klajite.

	Cu1	Cu2	As1	As2	Mn	Σ BV	H1	H2	H3	Σ BV + H	Anion
O1	0.38			1.14		1.52				1.52	O
O2			1.41			1.41				1.75	O
O3		0.14	1.06			1.20	0.70	0.23	0.11	1.90	OH
O4					$0.30 \times 2 \downarrow \rightarrow$	0.60				0.60	H ₂ O
O5		0.47				0.47				0.47	H ₂ O
O6				1.38	$0.30 \times 2 \downarrow \rightarrow$	1.98				1.98	O
O7	0.10					0.10				0.10	H ₂ O
O8	0.42, 0.45		1.23			2.10				2.10	O
O9						0.00	0.08	0.70	0.70	1.48	H ₂ O
O10					$0.28 \times 2 \downarrow \rightarrow$	0.56				0.56	H ₂ O
O11		0.41, 0.50		1.21		2.10				2.10	O
O12	0.47	0.16	1.28			1.91				1.91	O
O13	0.14	0.47		1.30		1.91				1.91	O
Σ BV	1.96	2.15	4.98	5.03	1.76		0.78	0.93	0.81		

All values are in valence units (vu). Cu–O, As–O, Mn–O bond strengths taken from Brown and Altermatt (1985), H–O bond strength taken from Brown (2002).

series the unit-cell volume V ranges from ~540 to ~560 Å³ (except for chudobaite, which has a smaller volume; Dorner and Weber, 1976), whilst in the case of lindackerites the volume varies at around ~520 Å³. The main differences lie in the c parameter, which is connected to the interplanar distance between the copper-arsenate sheets.

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