Kapellasite, $Cu_3Zn(OH)_6Cl_2$,
a new mineral from Lavrion, Greece, and its crystal structure

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ABSTRACT

Kapellasite, $Cu_3Zn(OH)_6Cl_2$, is a new secondary mineral from the Sounion No. 19 mine, Kamariza, Lavrion, Greece. It is a polymorph of herbertsmithite. Kapellasite forms crusts and small aggregates up to 0.5 mm, composed of bladed or needle-like indistinct crystals up to 0.2 mm long. The colour is green-blue, the streak is light green-blue. There is a good cleavage parallel to {0001}. Kapellasite is uniaxial negative, $\omega = 1.80(1)$, $\varepsilon = 1.76(1)$; pleochroism is distinct, with E = pale green, O = green-blue. $D_{meas} = 3.55(10)$ g/cm^3; $D_{calc.} = 3.62$ g/cm^3. Electron microprobe analyses of the type material gave CuO 58.86, ZnO 13.92, NiO 0.03, CoO 0.03, Fe$_2$O$_3$ 0.04, Cl 16.70, H$_2$O (calc.) 12.22, total 101.80, less O = Cl 3.77, total 98.03 wt.%. The empirical formula is $(Cu_{3.24}Zn_{0.75})_{\Sigma 3.99}(OH)_{5.94}Cl_{2.06}$, based on 8 anions. The five strongest XRD lines are [d in Å (I/I_0, hkl)] 5.730 (100, 001), 2.865 (11, 002), 2.730 (4, 200), 2.464 (9, 021/201), 1.976 (5, 022/202). Kapellasite is trigonal, space group $P\bar{3}m1$, unit-cell parameters (from single-crystal data) $a = 6.300(1)$, $c = 5.733(1)$ Å, $V = 197.06(6)$ Å^3, $Z = 1$. The crystal structure of kapellasite is based on brucite-like sheets parallel to (0001), built from edge-sharing distorted $M(OH,Cl)_6$ (M = Cu, Zn) octahedra. The sheets stack directly on each other (...AAA... stacking). Bonding between adjacent sheets is only due to weak hydrogen and O···Cl bonds. The name is in honour of Christo Kapellas (1938−2004), collector and mineral dealer from Kamariza, Lavrion, Greece.

KEYWORDS: kapellasite, new mineral, copper zinc hydroxide chloride, electron microprobe data, crystal structure, Lavrion, Greece.

Introduction

IN 1986 samples of green-blue crystal aggregates, labelled as botallackite, from the Juliushütte near Goslar, Harz mountains, Germany, were submitted to the first author for a preliminary investigation. It soon became clear that this material was probably a new copper zinc hydroxide chloride. Although its X-ray powder diffraction pattern showed some similarities to that of botallackite, there were also distinct differences and a refinement of the X-ray powder diffraction data based on the monoclinic botallackite unit cell was impossible. Tentative indexing of the powder data (Visser, 1969) gave a small hexagonal unit cell with $a = 6.3$ and $c = 5.7$ Å. Subsequently, the new phase was described in a collectors' journal as "botallackite", assuming that the differences in the powder diffraction pattern were due to the incorporation of zinc (Schnorrer-Köhler, 1987). Since the material formed in slags, further investigation and submission as a new mineral did not offer much promise, because at that time the International Mineralogical Assocation's Commission on New Minerals and Mineral Names were discussing the status of 'slag

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minerals'. This discussion finally resulted in the decision that secondary formations in slags could not be regarded as minerals (Nickel, 1995).

Approximately 12 years after the preliminary studies an obviously identical material was found in Lavrion, Greece – this time not in slags (Wendel *et al.*, 1999). Samples of the new find served for a complete characterization of the new species, approved in 2005 (IMA 2005-009). Type material is preserved in the collection of the Mineralogical Institute, University of Bochum, Germany, under catalogue number IMA-2005-009. The name is in honour of Christo Kapellas (1938−2004), collector and mineral dealer from Kamariza, Lavrion, Greece, one of the foremost experts on the Lavrion mineral assemblage. His extensive mineral collection is now part of the Lavrion Mineral Museum.

Occurrence

The type locality for kapellasite is the Sounion No. 19 mine (also incorrectly known as 'Chlorid-Stollen' by German collectors), Kamariza, Lavrion, Greece, where it forms crusts and small aggregates up to 0.5 mm, composed of bladed or needle-like indistinct crystals up to 0.2 mm long. The mineral, collected underground, formed from weathering of copper- and zinc-containing ore material, in the presence of chloride ions. Kapellasite occurs as one of the youngest phases on nearly completely oxidized ore material, almost always in association with gypsum. Other associated minerals include paratacamite, atacamite, gordaite, beaverite, hydrozincite and smithsonite. Rare members of this paragenesis are glaucocerinite, plumbojarosite, bianchite, herbertsmithite, anglesite, cumengéite, serpierite, ktenasite, calcite, quartz, pyrite and galena.
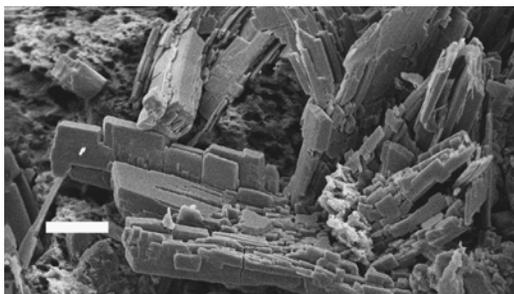
Kapellasite from the Juliushütte near Goslar, Harz mountains, Germany, is similar in appearance to the type locality material, except for the fact that it occurs in slags and therefore cannot be regarded as a mineral. However, samples from the Juliushütte have provided much useful data and will therefore be discussed in the present paper. Associated species at the Juliushütte are cumengéite, diaboleite and gypsum.

Physical data

Kapellasite forms crusts and small aggregates up to 0.5 mm, composed of indistinct green-blue crystals up to 0.2 mm long (Figs 1, 2). It is transparent and non-fluorescent in either long- or shortwave ultraviolet radiation; the lustre is adamantine and the streak is light green-blue. Vickers microhardness is $VHN_{25} = 200(30)$ kg/mm^2, corresponding to a Mohs hardness of 4. Kapellasite is brittle with an uneven fracture; it has a good cleavage parallel to {0001}, as derived from texture effects in the powder-diffraction pattern and from crystal-structure considerations. Most crystals exhibit a bladed or needle-like irregular habit and are typically strongly distorted with elongation perpendicular to [0001] (Fig. 3). Crystallographic forms are {0001} and {10$\bar{1}$0}. Trigonal symmetry is not readily apparent from the crystal morphology with the exception of one single sample from the Juliushütte that shows needle-like crystals elongated parallel to [0001] with a perfect trigonal {0001} termination (Fig. 4). Many crystal fragments are tabular on {10$\bar{1}$0}, thus showing a considerable birefringence when lying on {10$\bar{1}$0}. No twinning was observed. The density is 3.55(10) g/cm^3 and was measured by flotation in Clerici solution; the calculated density is

FIG. 1. SEM image of kapellasite crystals from Lavrion, Greece (type material). The scale bar is 20 µm long.

FIG. 2. SEM image of a kapellasite crystal aggregate in slags of the Juliushütte near Goslar, Harz mountains, Germany. The scale bar is 20 µm long.
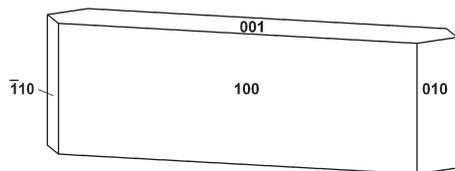
FIG. 3. Kapellasite crystal drawing; the tabular crystal is strongly distorted due to elongation perpendicular to [0001].
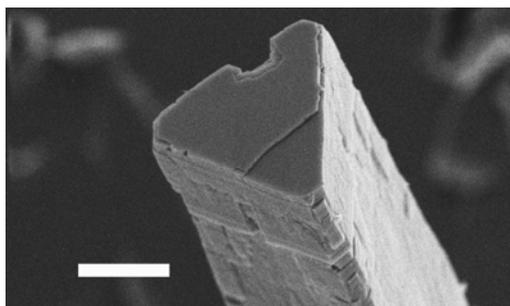
FIG. 4. SEM image of a kapellasite single crystal elongated parallel to [0001], in slags of the Juliushütte near Goslar, Harz mountains, Germany. The scale bar is 10 μm long.

3.62 g/cm^3 (based on the empirical formula and single-crystal data). Kapellasite is uniaxial negative with $\omega = 1.80(1)$ and $\varepsilon = 1.76(1)$ (measured at 589 nm). Pleochroism is distinct, with E = pale green and O = green-blue. Some crystals also show biaxial behaviour with 2V up to 20°.

Chemical and spectroscopic data

An electron microprobe (Cameca CAMEBAX, 10 nA, 20 kV, beam diameter 10 μm) was used for chemical analyses; analytical results and standards are given in Table 1. A possible chlorine loss induced by the electron beam was not observed. No other elements with atomic numbers >8 could be detected. There is a distinct solid solution involving copper and zinc. The mean total of (CuO+ZnO) is 72.78 wt.% with a standard deviation of 0.73, comprising 58.86 wt.% ± 2.71 for CuO and 13.92 wt.% ± 2.43 for ZnO, respectively. Water could not be

determined experimentally due to lack of material. It was calculated in order to achieve 8.0 anions (oxygen + chlorine) to conform with the results of the crystal-structure determination. The empirical formula (based on 8 anions p.f.u.) of the type material is $(Cu_{3.24}Zn_{0.75})_{\Sigma 3.99}(OH)_{5.94}Cl_{2.06}$ with ideal formula $Cu_3Zn(OH)_6Cl_2$. The composition of the material from the Juliushütte is closer to the ideal formula with zinc slightly exceeding unity in the formula unit (see Table 1, footnote 3). In addition, the range of CuO and ZnO is distinctly smaller, and the solid solution effect less pronounced than in the type material. Kapellasite easily dissolves in dilute mineral acids without effervescence. The compatibility index according to the Gladstone-

TABLE 1. EMPA[1] (wt.%) of kapellasite.

		Type material			Juliushütte (sample JU15)		
	mean[2]	range	e.s.d.		mean[3]	range	e.s.d.
CuO	58.86	54.77−61.72	2.71		52.80	52.03−54.20	0.74
ZnO	13.92	10.83−18.18	2.43		20.44	19.63−21.14	0.56
NiO	0.03	0.00−0.07	0.02		<0.05		
CoO	0.03	0.00−0.05	0.02		<0.05		
Fe$_2$O$_3$	0.04	0.00−0.12	0.03		<0.05		
Cl	16.70	16.36−16.96	0.20		16.58	16.18−16.98	0.24
H$_2$O[4]	12.22				12.27		
less O≡Cl	3.77				3.74		
Total	98.03				98.35		

[1] Microprobe standards: CuS (Cu), ZnO (Zn), NaCl (Cl), andradite (Fe), NiO (Ni), Co metal (Co).
[2] Means of nine sets of electron-microprobe analyses; empirical formula: $(Cu_{3.24}Zn_{0.75})_{\Sigma 3.99}(OH)_{5.94}Cl_{2.06}$.
[3] Means of 14 sets of electron microprobe analyses; empirical formula: $(Cu_{2.90}Zn_{1.10})_{\Sigma 4.00}(OH)_{5.96}Cl_{2.04}$.
[4] H$_2$O was calculated in order to achieve 8.0 anions (oxygen + chlorine) according to the results of the crystal-structure determination.
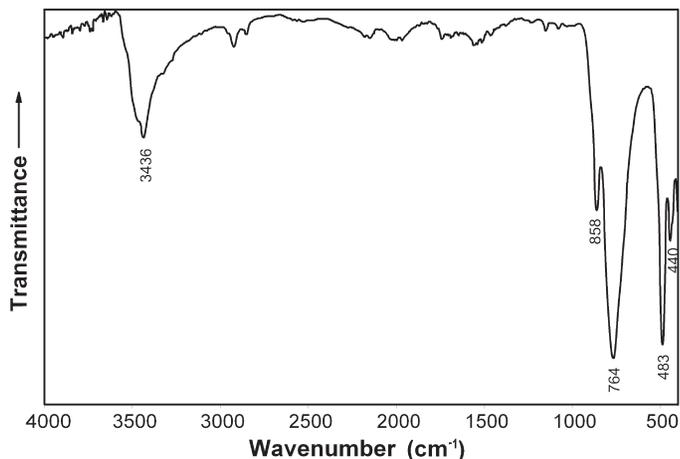
FIG. 5. IR spectrum of kapellasite (type material).

Dale relationship (Mandarino, 1981) is −0.018 (rated as superior). In addition to the crystal structure data the presence of hydroxyl groups could also be confirmed by Fourier-transform infrared spectra (FTIR) (Fig. 5). The IR data of kapellasite from the type locality and from the Juliushütte are compiled in Table 2 together with data for herbertsmithite and botallackite. All three species can be easily distinguished by means of IR spectroscopy, not only by different O−H stretching vibrations, but also by characteristic absorptions between 850 and 400 cm^{-1} involving metal−O−H bonds.

The bromide analogue of kapellasite has been synthesized by one of us (Braithwaite et al., 2004). Its X-ray powder pattern (M. Jones, University of Manchester) shows a set of lines related to those of kapellasite, but shifted and somewhat altered, which can be indexed on an expanded and distorted triclinic cell with $a = 5.5981$, $b = 6.0808$, $c = 6.3101$ Å, $\alpha = 90.250$, $\beta = 90.339$, $\gamma = 88.209°$, $V = 214.69$ Å^3. The FTIR spectrum of this phase is similar to that of kapellasite, with shifts in wavenumbers of vibrations affected by the substitution of chloride by the larger bromide ion and the consequent expansion of the lattice parameters. The resulting reduction in hydrogen bonding increases the wavenumbers of the O−H-stretching vibrations to 3542 (ms, sp) and 3500 (vs, sp) cm^{-1}. The O−H deformation wavenumbers are decreased to 845 (ms) and 719 (vs) cm^{-1}. The metal−O stretch at 483 cm^{-1} is unaffected. The other probable metal−O stretch is at 428 (ms, sp) cm^{-1}, between the values obtained for the

Lavrion and Juliushütte samples. This is unlikely to be a metal−halogen vibration, which would be expected to show a much larger decrease in wavenumber of ~100 cm^{-1}.

Single-crystal laser-Raman spectra of kapellasite were recorded in the range from 4000 to 200 cm^{-1} with a Renishaw M1000 MicroRaman Imaging System using a laser wavelength of 633 nm and excitation through a Leica DMLM optical microscope (unpolarized laser light, 180° backscatter mode, spectral resolution ± 2 cm^{-1}, minimum lateral resolution ~2 μm, random sample orientation). The crystals were only stable under the laser beam when the power was reduced to 25%; this is not unexpected for a green mineral absorbing a red laser light. A spectrum of reasonable quality showed bands at 3457 (O−H stretch), ~908 (vw), 481, 409, 326, ~279 to ~266 (both forming broad shoulders), 247 and ~232 cm^{-1}. These bands allow an easy differentiation between kapellasite and botallackite or herbertsmithite. The fact that the IR and Raman bands of kapellasite do not coincide confirms the centrosymmetry of the crystal structure (mutual exclusion rule).

Kapellasite, ideally $Cu_3Zn(OH)_6Cl_2$, is a polymorph of herbertsmithite, and closely related to the $Cu_2(OH)_3Cl$ polymorphs. The synthesis of the latter has been studied by a number of authors (Feitknecht and Maget, 1949a; Oswald and Feitknecht, 1964; Pollard et al., 1989; Jambor et al., 1996). These studies also include compounds of the general formula $M_2(OH)_3Cl$ where M is a cation similar to Cu^{2+}, such as Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+} and Fe^{2+}. Feitknecht and

TABLE 2. Wavenumbers (cm^{-1}) of IR absorption maxima[1] for kapellasite, herbertsmithite and botallackite.

(1)	(2)	(3)	(4)	Comments
~3480 sh	3490 sh		3520 s, sp	O−H stretch
	3475 vs, sp			O−H stretch
3436 s, sp	3446 ms, sp	3410 sh	3440 sh	O−H stretch
		3380 vs, sp	3420 s	O−H stretch
		3320 sh		O−H stretch
	976 fw	970 sh		O−H deformations?
	941 w	945 s, fsp		O−H deformations?
858 m	856 m		853 s	O−H deformations
			815 s, sp	O−H deformations
764 vs, fsp	766 vs, fsp	753 s, br	778 s, fbr	O−H deformations
	735 w sh, imp?	703 s, fbr	O−H deformations	
	600 w	597 w, br		Metal−O stretch?
			525 s, sp	Metal−O stretch?
			502 s, sp	Metal−O stretch?
483 s	481 s	460 s	450 ms, sp	Metal−O stretch?
440 m, sp	419 m, sp		418 s	Metal−O stretch?

[1] s = strong, m = medium, w = weak, sh = shoulder, sp = sharp, br = broad, v = very, f = fairly, imp = impurity absorption.
Spectrum 1 measured by E. Jaegers in a diamond microcell, using a Nicolet 5PC Fourier transform infrared spectrometer.
Spectra 2−4 measured by R.S.W. Braithwaite at University of Manchester, in nujol mulls between KBr plates, using a Philips Analytical PU 9600 Fourier transform infrared spectrometer.
(1) Kapellasite, Sounion, Kamariza, Greece; sample WEN008 (type material). See Fig. 5.
(2) Kapellasite, Juliushütte, Goslar, Harz mountains, Germany. Blue-green blades off RSWB 91-113, collected and presented by Dr G. Jung.
(3) Herbertsmithite, Mina de Los Tres Presidentes, Chile; Cu/Zn = 3/1. Type material (Braithwaite et al., 2004).
(4) Botallackite, Levant mine, Cornwall, England. Off RSWB 74-244, collected and presented by the late R.W. Barstow.

Maget (1949b) showed that a quarter of the Cu cations can be replaced with other cations resulting in so-called double salts of the formula $Cu_3M(OH)_6Cl_2$, with $M = Ni^{2+}$, Co^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+}. The first naturally occurring example of this series is herbertsmithite, $Cu_3Zn(OH)_6Cl_2$ (Braithwaite et al., 2004). Using zinc chloride solutions and copper powder, Feitknecht and Maget (1949b) synthesized two different copper zinc hydroxide chlorides, called IIγ (identical with herbertsmithite) and IIα. The stable end product at all investigated concentrations turned out to be IIγ, whereas IIα is more or less unstable and was only observed at medium concentrations of zinc chloride. According to electron microscopic investigations (Feitknecht and Maget, 1949b), IIα formed well developed hexagonal tabular crystals; its powder diffraction pattern could be indexed with a small hexagonal unit cell. Feitknecht and Maget (1949b) attributed this phase to the so-called 'C6 type' which was also found for a number of synthetic compounds of the formula $M_2(OH)_3Cl$ with $M = Co^{2+}$, Fe^{2+}, Mn^{2+}, Ni^{2+} and Mg^{2+} (Oswalt and Feitknecht, 1964). They proposed space group $P\bar{3}m1$ for compounds of the C6 type, assuming statistically distributed hydroxyl and chloride ions. Unfortunately, Feitknecht and Maget (1949b) gave no numerical X-ray powder diffraction data for IIα but only a rough line drawing of the X-ray powder pattern, which is in fact very similar to the pattern of kapellasite. It is therefore most likely that the synthetic phase IIα is identical with kapellasite.

X-ray diffraction

X-ray powder diffraction

Guinier and powder diffractometer measurements (Table 3) were taken from a number of different samples from Lavrion, Greece and from the

TABLE 3. X-ray powder diffraction data of kapellasite[1].

h	k	i	l	d_{calc}	I_{calc}	d_{obs}	I_{obs}	$I_{obs\ (corr)}$[2]
0	0	0	1	5.727	100	5.730	100	100
1	0	$\bar{1}$	0	5.458	3	5.474	1	6
1	0	$\bar{1}$	1	3.951	5	3.951	1	7
1	1	$\bar{2}$	0	3.150	2	not observed		
0	0	0	2	2.864	11	2.865	11	11
1	1	$\bar{2}$	1	2.761	3	2.761	1	12
1	1	$\bar{2}$	$\bar{1}$	2.761	3			
2	0	$\bar{2}$	0	2.729	19	2.730	4	39
0	1	$\bar{1}$	2	2.536	5	2.533	2	6
1	0	$\bar{1}$	2	2.536	4			
0	2	$\bar{2}$	1	2.463	66	2.464	9	81
2	0	$\bar{2}$	1	2.463	9			
0	2	$\bar{2}$	2	1.976	22	1.976	5	32
2	0	$\bar{2}$	2	1.976	18			
0	0	0	3	1.909	4	1.910	4	4
2	2	$\bar{4}$	0	1.575	21	1.576	2	17
0	2	$\bar{2}$	3	1.564	13	1.565	2	9
2	0	$\bar{2}$	3	1.564	6			
2	2	$\bar{4}$	1	1.519	8	1.519	1	10
2	2	$\bar{4}$	$\bar{1}$	1.519	8			
2	2	$\bar{4}$	2	1.380	4	1.380	1	8
2	2	$\bar{4}$	$\bar{2}$	1.380	4			
4	0	$\bar{4}$	0	1.365	3	not observed		
0	4	$\bar{4}$	1	1.327	2	1.527	1	8
4	0	$\bar{4}$	1	1.327	10			
0	2	$\bar{2}$	4	1.268	6	1.268	1	3
2	0	$\bar{2}$	4	1.268	9			
0	4	$\bar{4}$	2	1.232	5	1.232	1	6
4	0	$\bar{4}$	2	1.232	5			

[1] Philips X'Pert powder diffractometer, Cu-$K\alpha$ radiation; reflection mode; internal standard: Si. I_{calc} calculated using *LAZY PULVERIX* (Yvon *et al.*, 1977); reflections with $I_{calc} \geqslant 2$ are listed.
[2] The powder diffraction pattern shows strong texture effects due to preferred orientation parallel to {0001}. Observed intensities I_{obs} are not corrected for texture effects. Intensities $I_{obs\ (corr.)}$ are corrected according to the March model (Deyu *et al.*, 1990); March coefficient 0.59.

Juliushütte near Goslar, Germany. All samples show sharp diffraction lines and apart from distinct texture effects, due to preferred orientation parallel to {0001}, no significant differences could be observed; the refined unit-cell parameters are close (Table 4). The X-ray powder-diffraction pattern of kapellasite is somewhat similar to that of botallackite, and both minerals might have been confused in the past.

Single-crystal X-ray diffraction

Due to the poor crystal quality and small crystal size it was difficult to find fragments suitable for single-crystal investigations and in particular for a structure determination. This was considered the crucial point in determining the correct symmetry, because the powder patterns could be equally refined in either trigonal/hexagonal, orthorhombic or monoclinic unit cells. After several attempts, a very small crystal fragment of the Juliushütte material was found to be suitable for the determination of the crystal structure. Subsequently, equivalent structural data could also be obtained from a tiny crystal of the type material. The single-crystal X-ray intensity data were collected at 293 K (type material, at Vienna) and 150 K (Juliushütte material, at Manchester), using two different single-crystal X-ray diffractometers each equipped with a CCD area detector

TABLE 4. Refined unit-cell parameters of kapellasite.

a	c	V	Sample	Description
6.300(1)	5.733(1)	197.06(6)	WEN008	type material, refined from single-crystal data
6.3019(10)	5.7275(11)	196.99(6)	WEN008	type material, refined from powder data
6.2990(7)	5.7278(11)	196.82(5)	WEN018	Lavrion, refined from powder data
6.309(1)	5.745(1)	198.03(6)	C25-1	Juliushütte, refined from single-crystal data
6.3032(11)	5.7035(11)	196.24(7)	RSWB 91-113	Juliushütte, refined from single-crystal data[1]
6.3076(9)	5.7276(8)	197.35(6)	JU15	Juliushütte, refined from powder data

[1] At 150(2) K (note decreased c parameter).

(Mo-$K\alpha$ radiation). Details of the data collection at 293 K are compiled in Table 5 (only the results obtained for the type material will be presented here because the residual of the refinement is distinctly lower). The structure was solved and refined in space group $P\bar{3}m1$ using *SHELXS97* and *SHELXL97*, respectively (Sheldrick, 1997*a,b*) to final $R(F)$ values of 2.6 and 4.7%, respectively. The hydrogen atom could not be detected. Refined unit-cell parameters are given in Tables 4 and 5. The final positional and displacement parameters of the type material are given in Table 6.

TABLE 5. Crystal data, data collection information and refinement details for type kapellasite.

Crystal data:	
Formula	$Cu_3ZnCl_2(OH_{5.82}Cl_{0.18})$
Space group, Z	$P\bar{3}m1$ (no. 164), 1
a, c (Å)	6.300(1), 5.733(1)
V (Å^3)	197.06(6)
$F(000)$, ρ_{calc} (g cm^{-3})	206, 3.64
μ (mm^{-1})	11.71
Absorption correction	multi-scan*
Crystal dimensions (mm)	$0.015 \times 0.03 \times 0.06$
Data collection and refinement:	
Diffractometer	Nonius KappaCCD system
λ (Mo-$K\alpha$) (Å), T (K)	0.71073, 293
Crystal$-$detector distance (mm)	26
Rotation axis, width (º)	ω, 2
Total no. of frames	196
Collection time per degree (s)	360
Collection mode, $2\theta_{max}$ (º)	sphere (redundancy 0.5), 55
h, k, l ranges	$-8 \rightarrow 8$, $-8 \rightarrow 8$, $-7 \rightarrow 7$
Total reflections measured	1612
Unique reflections	195 (R_{int} 4.7%)
$R1(F)$, w$R2_{all}(F^2)$**	2.57%, 3.62%
'Observed' reflections	154 [$F_o > 4\sigma(F_o)$]
Extinction coefficient	0.007(3)
Number of refined parameters	20
GooF	1.166
$(\Delta/\sigma)_{max}$	0.000
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	-0.56, 0.99

Unit-cell parameters were refined from 840 recorded reflections.
Scattering factors for neutral atoms were employed in the refinement.
* Otwinowski *et al.* (2003)
** w = $1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.25P]$; P = $([max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$

TABLE 6. Fractional atomic coordinates and displacement parameters ($\mathring{A}^2$) for type kapellasite[1].

Atom	x	y	z	U_{eq}
Cu	0.5	0.0	0.5	0.0165(4)
Zn	0.0	0.0	0.5	0.0176(4)
O (OH)[2]	0.3544(6)	0.1772(3)	0.3454(6)	0.0161(9)
Cl[3]	0.33333	−0.33333	0.1373(4)	0.0251(6)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	0.0130(5)	0.0153(6)	0.0221(5)	0.0012(4)	0.00060(18)	0.0076(3)
Zn	0.0134(5)	0.0134(5)	0.0259(8)	0.0	0.0	0.0067(3)
O (OH)	0.0179(19)	0.0155(14)	0.0158(18)	−0.0006(7)	−0.0012(14)	0.0090(9)
Cl	0.0276(8)	0.0276(8)	0.0200(10)	0.0	0.0	0.0138(4)

[1] Only values obtained from the dataset collected at 293 K are shown.
[2] About 3% of the OH^- group is replaced by a Cl^- anion (refined occupancy: $OH_{0.971(5)}Cl_{0.029(5)}$), which is located at a site with the coordinates 0.359(8), 0.180(4), 0.160(7) (U_{iso} fixed at 0.02 $\mathring{A}^2$).
[3] The Cl site is fully occupied (refined occupancy 0.99).

Description of the crystal structure

The asymmetric unit of kapellasite contains one Cu, one Zn, one O and one Cl atom. The crystal structure of kapellasite is based on brucite-like sheets parallel to (0001) built from edge-sharing angle-distorted $Zn(OH)_6$ and Jahn-Teller distorted $Cu(OH)_4Cl_2$ octahedra (Figs 6, 7). Since the Cu atom has four O ligands and two Cl ligands, the bonds are necessarily different. The geometry is as expected for Cu in such environments. The sheets stack directly on each other (...*AAA*... stacking). Bonding between adjacent sheets is only by weak hydrogen and O···Cl bonds. Refined metal−anion bond lengths are as follows: Zn−O = 2.127(3) Å (6×), Cu−O = 1.974(2) Å (4×) and Cu−Cl = 2.7624(19) Å (2×) (Table 7).

A very small amount of the O atom (~3%) is replaced by Cl (Table 6), and the refined Cl:OH ratios in the two measured crystals are also very
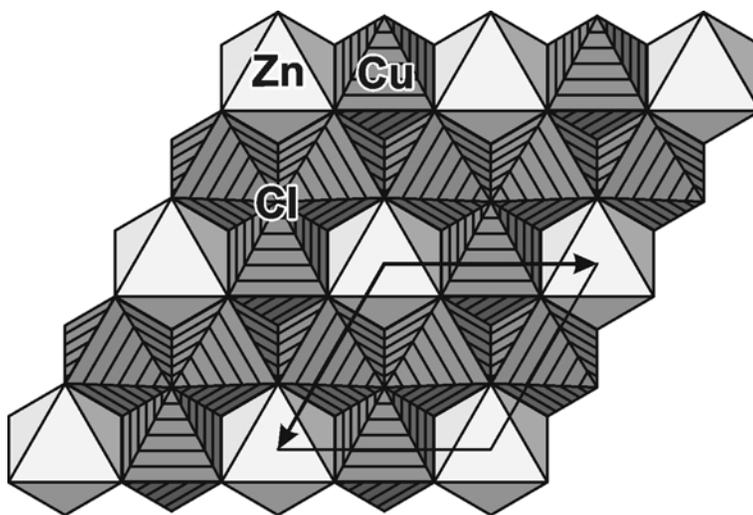
FIG. 6. The crystal structure of kapellasite in a view along the *c* axis.
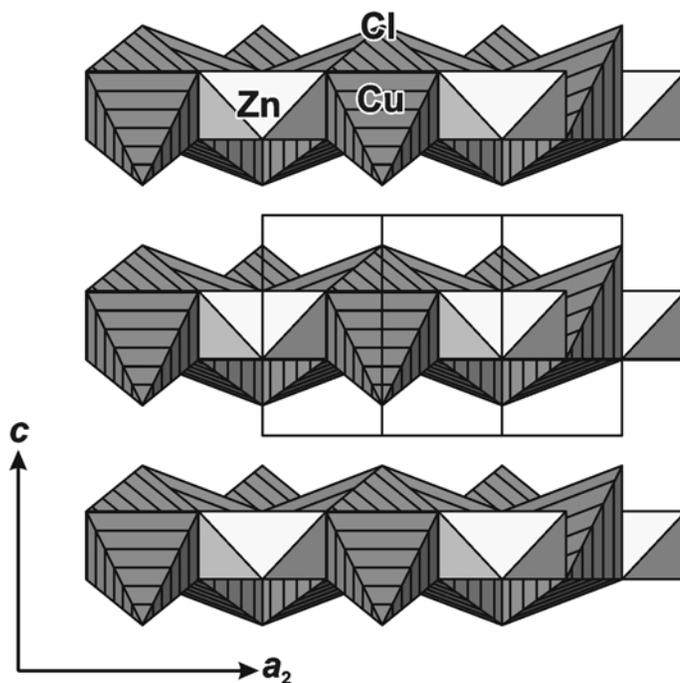
FIG. 7. The crystal structure of kapellasite in a view along the a^* axis. Note the considerable distortion of the $Zn(OH)_6$ and $Cu-(O,Cl)$ 'octahedra', and the stacking sequence ...*AAA*... .

slightly different. Calculated bond-valence sums for the atoms (Table 7) are close to ideal values.

Discussion

Kapellasite is a polymorph of herbertsmithite, and closely related to paratacamite, atacamite, clino-atacamite and botallackite; see Table 8 for a comparison of the relevant data. The crystal structures within this group of copper (zinc) hydroxide chlorides can be assigned to two different types: (1) layer structures (botallackite, kapellasite); and (2) structures with a three-dimensional framework (atacamite, paratacamite,

TABLE 7. Selected bond distances (Å), bond angles (º) and calculated bond valences (vu)[1] for the coordination polyhedra in kapellasite.

Zn−O (×6)	2.127(3)	0.318 vu	Cu−O (×4)	1.974(2)	0.451 vu
			Cu−Cl (×2)	2.7624(19)	0.095 vu
<Zn−O>	2.127	1.91 vu	<Cu−O>	2.237	1.99 vu
O−Zn−O	180.0(2)		O−Cu−O (×2)	180.0	
O−Zn−O (×6)	103.86(11)		O−Cu−O (×2)	83.28(19)	
O−Zn−O (×6)	76.14(11)		O−Cu−O (×2)	96.72(19)	
O−Zn−O (×2)	180.0		O−Cu−Cl (×4)	89.11(9)	
			O−Cu−Cl (×4)	90.89(9)	
			Cl−Cu−Cl	180.00(7)	

[1] Bond-valence sums (vu) for O (= OH) and Cl are 1.22 and 0.29 vu, respectively. Bond-valence sums for Cl in copper/zinc hydroxide chlorides are known to be anomalously low (e.g. Grice *et al*., 1996).
Bond-valence parameters used are from Brown (1996; updated values from www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown) (Cu-Cl parameters) and Brese and O'Keeffe (1991) (remaining parameters).

TABLE 8. Comparison of data for kapellasite and related minerals.

	Atacamite	Clinoatacamite	Botallackite	Paratacamite	Herbertsmithite	Kapellasite
Chemical formula	$Cu_2(OH)_3Cl$	$Cu_2(OH)_3Cl$	$Cu_2(OH)_3Cl$	$Cu_3(Cu,Zn)(OH)_6Cl_2$	$Cu_3Zn(OH)_6Cl_2$	$Cu_3Zn(OH)_6Cl_2$
Crystal system	orthorhombic	monoclinic	monoclinic	trigonal	trigonal	trigonal
Space group	$Pnma$	$P2_1/n$	$P2_1/m$	$R\bar{3}$	$R\bar{3}m$	$P\bar{3}m1$
a (Å)	6.030	6.144	5.717	13.654	6.834	6.302
b (Å)	6.865	6.805	6.126			
c (Å)	9.120	9.112	5.636	14.041	14.075	5.727
β (°)		99.55	93.07			
V (Å³)	377.5	375.7	197.1	2267	569.3	197.0
Z	4	4	2	12	3	1
Specific volume [1] (Å³)	94.4	93.9	98.6	94.5	94.9	98.5
D_x (g/cm³)	3.76	3.78	3.60	3.76	3.75	3.62
$d1$ (Å) (I/I_o) [2]	5.485 (100)	5.461 (100)	5.709 (100)	5.449 (100)	5.466 (55)	5.727 (100)
$d2$ (Å) (I/I_o) [2]	5.030 (73)	2.766 (43)	2.579 (26)	2.758 (84)	2.764 (100)	2.464 (66)
$d3$ (Å) (I/I_o) [2]	2.835 (63)	2.263 (63)	2.410 (41)	2.261 (64)	2.266 (30)	1.976 (22)
Optical character	biaxial (−)	biaxial (−)	biaxial (+)	uniaxial (−)	uniaxial (−)	uniaxial (−)
Structure reference	Parise and Hyde (1986)	Grice et al. (1996)	Hawthorne (1985)	Fleet (1975)	Braithwaite et al. (2004)	this work

[1] Specific volume for one $M_2(OH)_3Cl$ unit.
[2] $d1$, $d2$, $d3$: strongest reflections in the calculated X-ray powder-diffraction pattern.

clinoatacamite, herbertsmithite). Both types are distinctly different regarding density and stability. Botallackite and kapellasite have densities of ~ 3.6 g/cm^3, whereas the other species show distinctly higher values of ~ 3.75 g/cm^3. The different packing density is also indicated by the specific volume required for one $M_2(OH)_3Cl$ unit (M = Cu, Zn). This is ~ 98.5 Å^3 for botallackite and kapellasite compared with only 94 to 95 Å^3 for atacamite, paratacamite, clinoatacamite and herbertsmithite (Table 8). In addition, the basal reflection or its equivalent in the X-ray powder diffraction pattern, an indication for the layer distance in the crystal structure, is ~ 5.7 Å for botallackite and kapellasite and only ~ 5.45 Å for the other species. The enhanced layer distance and the lower packing density are indications of a lower stability of botallackite and kapellasite, and in agreement with the observations of Feitknecht and Maget (1949b) on synthetic material (see above). The existence of synthetic $Cu_3M(OH)_6Cl_2$ (M = Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+}) compounds (Feitknecht and Maget, 1949b) suggest that chemical analogues of kapellasite may be found in nature in environments strongly depleted in zinc.

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