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Ktenasite, another mineral with $^2_\infty[(\mathrm{Cu,Zn})_2(\mathrm{OH})_3\mathrm{O}]^-$ octahedral sheets

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Abstract

The crystal structure of ktenasite from Miniera Trentin (space group $P2_1/c$, $a = 5.589$, $b = 6.166$, $c = 23.751$ Å, $\beta = 95.55°$) was determined by Patterson and Fourier methods and refined to a final R value of 0.058.

The structure is characterized by corrugated sheets $^2_\infty[(\mathrm{Cu,Zn})_2(\mathrm{OH})_3\mathrm{O}]^-$ of distorted copper-zinc polyhedra. Sulphate groups are connected to both sides of the octahedral sheet by corner sharing. The resultant composite tetrahedral-octahedral layers are connected each other by $[\mathrm{Zn(H_2O)_6}]^{+2}$ octahedra through a system of hydrogen bonds. The crystal chemical formula for ktenasite from Miniera Trentin is

$$\mathrm{Zn_2(Cu_{5.2}Zn_{2.8})(SO_4)_4(OH)_{12} \cdot 12H_2O}.$$

The relations of ktenasite with other minerals are remarked and discussed.

Introduction

Ktenasite was first found by Kokkoros (1950) in the Kamariza Mine, Laurium (Greece); the mineral had monoclinic symmetry, space group $P2_1/c$, lattice parameters $a = 11.16$, $b = 6.11$, $c = 23.74$Å, $\beta = 95°24'$. The proposed formula

$$\mathrm{(Cu,Zn)_3SO_4(OH)_4 \cdot 2H_2O}$$

leads to a calculated density $D_{\mathrm{calc}} = 3.26$ g cm^{-3} in poor agreement with the observed density $D_{\mathrm{obs}} = 2.97$ g cm^{-3}.

Ktenasite was subsequently found in Ecton Mine, Montgomery County (Pennsylvania) (Rankin, 1969) and in 79 Mine, Gila Co. (Arizona): for both findings no data are given.

Recently, RAADE, ELLIOTT and FEJER (1977) described ktenasite from Glomsrudkollen zinc mine, Modum (Norway), as monoclinic, space group $P2_1/c$, cell dimensions $a = 5.598$, $b = 6.121$, $c = 23.762$ Å, $\beta = 95.55°$, with chemical formula

$$(Cu_{3.5}Zn_{1.5})(SO_4)_2(OH)_6 \cdot 6\,H_2O$$

$D_{obs} = 2.94$ and $D_{calc} = 2.96$ g cm^{-3}, for $Z = 2$. The main differences between Laurium and Modum samples are the halvening of the a parameter in the Modum mineral, a different Cu/Zn ratio and disagreement in the powder diffraction pattern, due, according to RAADE *et al.* (1977), to the presence of diffraction peaks of brochantite and smithsonite in the pattern of the Laurium mineral.

Ktenasite was also found in Miniera Trentin, Vicenza (Italy), by BOSCARDIN, MELLINI and ORLANDI (unpublished data). These authors observed the same a parameter as RAADE *et al.* (1977), powder diffraction pattern like that of ktenasite from Modum, no diffuse streaks in x-ray single crystal diffraction patterns and obtained analytical data leading to the unit cell content

$$Cu_{5.2}Zn_{4.8}(SO_4)_4(OH)_{12} \cdot 12\,H_2O\,,$$

with $D_{obs} = 2.98$ g cm^{-3} and $D_{calc} = 2.95$ g cm^{-3}. The chemical analysis of ktenasite from Miniera Trentin is in good agreement with the crystal chemical formula of RAADE *et al.* (1977), but the Cu/Zn ratio is nearly the same as given for ktenasite from Laurium by KOKKOROS (1950).

Experimental

A small crystal ($0.1 \times 0.13 \times 0.2$ mm^3) of ktenasite from Miniera Trentin was used for crystal structure determination. Weissenberg photographs showed monoclinic symmetry, with $P2_1/c$ space group. The lattice parameters were refined by least-squares fitting of 25 θ values, measured on the Philips PW 1100 single crystal automatic diffractometer, using Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å); their values were $a = 5.589(1)$, $b = 6.166(1)$, $c = 23.751(7)$ Å, $\beta = 95.55(1)°$. Intensity data were collected on the same diffractometer, using θ—2θ scan, scan width 3.0°, from 2° up to 65° θ, by Cu$K\alpha$ radiation. Two symmetry equivalents quadrants (*hkl* and $h\bar{k}l$ reflections) were measured and thereafter averaged, to give 1381 independent diffractions.

Among these, 171 were classified as "not observed", having F_o less than three times the corresponding standard deviation $\sigma(F_o)$, as estimated by counting statistics. No absorption correction was made, owing to the small dimensions of the crystal. In subsequent structure factors calculations, scattering factors for neutral atoms were taken from CROMER and MANN (1968).

Structure determination

A Patterson map led to locate three heavy atoms in the asymmetric unit; the first, hereafter named Zn atom, was at the origin, the others, Cu(1) and Cu(2), were disposed to build a pseudohexagonal sheet in the (001) plane, at $z \simeq 1/4$. Subsequent Fourier maps located the sulphur atom and all the oxygen atoms; the structure was refined by

Table 1. *Positional and thermal parameters for heavy atoms*, with e.s.d.'s in parentheses, and positional parameters for hydrogen atoms

	x	y	z
Zn	0.0	0.0	0.0
Cu(1)	−0.0106(2)	0.0995(2)	0.2490(1)
Cu(2)	0.4990(3)	−0.1508(3)	0.2470(1)
S	0.3600(5)	0.0571(5)	0.3738(1)
O(1)	0.3328(13)	0.0946(13)	0.3128(3)
O(2)	0.6073(13)	0.1049(13)	0.2096(3)
O(3)	0.8396(12)	0.3556(13)	0.2896(3)
O(4)	0.1635(13)	0.3440(13)	0.2149(3)
O(5)	0.1264(14)	−0.0071(15)	0.3927(3)
O(6)	0.4409(15)	0.2594(15)	0.4018(4)
O(7)	0.5385(15)	−0.1161(15)	0.3859(3)
O(8)	0.9163(15)	0.0626(15)	0.0827(3)
O(9)	0.3281(15)	0.1617(15)	0.0189(4)
O(10)	0.1436(15)	−0.2890(15)	0.0290(4)
H(2)	0.593	0.083	0.175
H(3)	0.856	0.350	0.328
H(4)	0.154	0.344	0.184
H(81)	0.989	0.031	0.103
H(82)	0.782	0.017	0.077
H(91)	0.363	0.078	0.016
H(92)	0.362	0.250	0.046
H(101)	0.202	−0.239	0.056
H(102)	0.042	−0.333	0.056

Table 1. *(Continued)*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.0149(7)	0.0141(6)	0.0008(1)	−0.0002(5)	0.0007(1)	0.0000(1)
Cu(1)	0098(4)	0096(4)	0010(1)	0001(4)	0007(1)	0001(1)
Cu(2)	0109(4)	0114(4)	0011(1)	− 0006(4)	0010(1)	0000(1)
S	0082(8)	0085(7)	0004(1)	0009(6)	0005(2)	− 0003(1)
O(1)	007(2)	011(2)	0006(1)	001(2)	0006(4)	0005(5)
O(2)	008(2)	011(2)	0005(1)	000(2)	0012(5)	0000(4)
O(3)	004(2)	012(2)	0006(1)	000(2)	0004(4)	0005(5)
O(4)	007(2)	012(2)	0005(1)	000(2)	0007(4)	0003(4)
O(5)	011(3)	016(3)	0010(2)	000(2)	0021(5)	0000(5)
O(6)	016(3)	013(3)	0014(2)	002(2)	− 0012(6)	− 0027(6)
O(7)	016(3)	013(3)	0008(2)	009(2)	0001(5)	0002(5)
O(8)	015(3)	017(3)	0007(1)	000(2)	0004(5)	− 0002(5)
O(9)	013(3)	016(3)	0010(2)	− 005(2)	0005(5)	− 0006(5)
O(10)	018(3)	014(3)	0008(2)	001(2)	0005(6)	0004(5)

Anisotropic thermal parameters are in the form:

$$\exp\left[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\right].$$

full-matrix least-squares cycles, with individual isotropic thermal parameters, to a value of the conventional factor $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.08. At this stage, a ΔF map showed the positions of all the hydrogen atoms. Further refinement cycles, with anisotropic thermal parameters for copper, zinc, sulphur and oxygen atoms, were made. A weighting scheme based on the reciprocal of the variance was used. The isotropic thermal ($B = 2.0$ Å^2) and positional parameters for the hydrogen atoms were not refined. The final R_1 and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$ values were 0.058 and 0.067 respectively. Final atomic positional and thermal parameters are given in Table 1. Observed and calculated structure factors were deposited at Akad. Verlagsgesellschaft, Wiesbaden.

Description and discussion of the structure

The crystal structure of ktenasite, as projected along [010], is illustrated in Fig. 1, where the structure is described in terms of Zn and Cu octahedra and sulphur tetrahedra. Bond lengths in these polyhedra are given in Table 2; the atoms of the different asymmetric

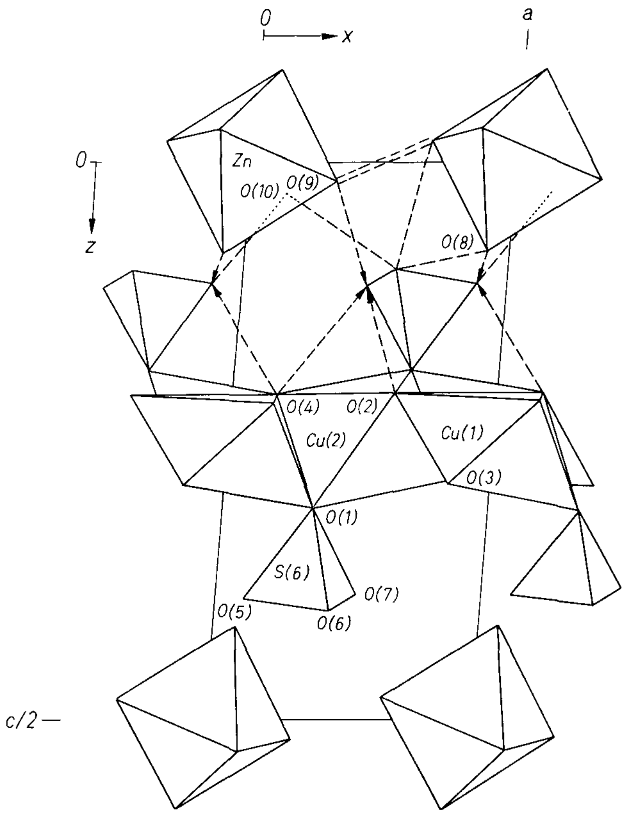

Fig. 1. Crystal structure of ktenasite, viewed along [010]. The dashed lines indicate hydrogen bonds: the arrows indicate bonding with atoms translated one unit in the [010] direction. The double dashed line joining O(9) and O(9)^{vi} atoms indicates the two hydrogen bonds O(9)—H(9)···O(9)^{vi} and O(9)^{vi}—H(9)^{vi}···O(9)

units are related by superscripts to the symmetry equivalent atoms of the fundamental unit as follows:

i	atom at	$-1+x$	y	z
ii	atom at	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
iii	atom at	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
iv	atom at	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
v	atom at	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
vi	atom at	$1-x$	$-y$	$-z$
vii	atom at	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

Table 2. *Bond distances* (Å) *in the coordination polyhedra*, with e.s.d.'s in parentheses

Cu(1)—O(1)	2.328(14)	Cu(2)—O(1)	2.424(10)
—O(2)^{i}	2.247(11)	—O(1)^{ii}	2.372(10)
—O(3)^{i}	2.069(9)	—O(4)^{ii}	2.012(11)
—O(3)^{ii}	2.046(9)	—O(3)^{ii}	2.005(11)
—O(4)^{iii}	2.023(9)	—O(2)^{ii}	1.950(9)
—O(4)	2.007(9)	—O(2)	1.936(9)
Zn—O(8)^{i}	2.098(9) × 2	S—O(1)	1.460(8)
—O(9)	2.098(9) × 2	—O(5)	1.475(10)
—O(10)	2.095(9) × 2	—O(6)	1.464(10)
		—O(7)	1.471(9)

Main feature is the presence of continuous sheets of octahedrally coordinated Cu(1) and Cu(2) cations; a tetrahedral sulphate group, repeated on both sides of the sheet by screw axis rotation, is linked to the sheet by corner sharing. As shown in Fig. 1, the octahedral sheet is corrugated, owing to the distortions of Cu(1) and Cu(2) polyhedra from the regular octahedron towards the elongated tetragonal bipyramid (Table 2): for Cu(1) site the equatorial bond distances range from 2.007 to 2.069 Å and the axial bond distances are 2.247 and 2.328 Å, for Cu(2) site the variation of equatorial distances is from 1.936 to 2.012 Å and the axial bond distances are 2.372 and 2.424 Å. Sandwiched between subsequent composite tetrahedral-octahedral layers are isolated Zn regular coordination octahedra. The Zn—O mean bond length (2.097 Å) compares very well with the value 2.105 Å calculated from the ionic radii of Shannon and Prewitt (1969). The observed coordination geometry of Cu(1), Cu(2) and Zn sites is easily explainable on the basis of the Jahn-Teller effect (Orgel and Dunitz, 1957).

As the chemical analysis indicates the presence of nearly five zinc atoms in the unit cell and only two of them can be accomodated in the Zn site, three zinc atoms are distributed in the distorted Cu(1) and Cu(2) octahedra. As the Cu(1) octahedron is less distorted, in that site copper atoms are probably replaced by zinc atoms at an higher degree than in Cu(2) site.

The question of the distribution of zinc and copper atoms among different octahedra arose also in the crystal structure analyses of serpierite $Ca(Cu,Zn)_4(OH)_6(SO_4)_2 \cdot 3H_2O$ (Sabelli and Zanazzi, 1968) and veszelyite $(Cu,Zn)_2ZnPO_4(OH)_3 \cdot 2H_2O$ (Ghose, Leo and Wan, 1974) and was similarly qualitatively answered on the basis of the different octahedral distortions of the various sites. Table 3 gives for the various octahedra in these structures the corresponding values of ΔL, where ΔL is the difference between the average values of axial and equatorial bond distances.

Table 3. Cu—Zn *contents calculated from the distortion of the octahedra, compared with the* Cu—Zn *contents from chemical analyses*

	Site	ΔL	Calculated Cu atoms	Calculated values	Analytical values	
	Zn	0.0	0.0	4.77	5.2	Cu
Ktenasite	Cu(1)	0.25	1.78	5.23	4.8	Zn
(present paper)	Cu(2)	0.42	2.99			
Veszelyite	Cu(1)	0.57	4.00	6.88	7.06	Cu
(Ghose *et al.*, 1974)	Cu(2)	0.41	2.88	1.12	0.94	Zn
	Cu(1)	0.17	2.41			
Serpierite	Cu(2)	0.47	6.66	20.61	21.10	Cu
(Sabelli and	Cu(3)	0.55	7.79	11.39	10.90	Zn
Zanazzi, 1972)	Cu(4)	0.01	0.07			
	Cu(5)	0.52	3.68			

It is tempting to calculate, on the basis of these values, the copper content in each site, assuming a linear correlation between the copper content and ΔL value, with $\Delta L = 0.0$ for 100% zinc and $\Delta L = 0.57$ [the maximum value in Table 3, for Cu(1) site in veszelyite] for 100% copper. The results of such a calculation are summarized in Table 3 which compares the calculated contens of copper and zinc atoms in the unit cell of the three minerals, with those obtained by the chemical analysis. Notwithstanding the good agreement we are aware of the weakness of an indiscriminate application of such an approach, mainly because it is well known that the unsubstituted copper octahedron undergoes different distortions in different crystal structures. However in this case such an approach could be justified by the presence in the three minerals of the common structural feature of

(Cu, Zn) octahedral sheet. In this connection it would be very interesting to compare Cu(1) and Cu(2) sites in ktenasite from Miniera Trentin with the corresponding sites in ktenasite from Modum, which has a lower zinc content. In such a case our approach could be confidently applied and reliable indications on the zinc distribution between the two independent Cu sites could be derived.

Hydrogen bond system

From a list of all the distances shorter than 3.10 Å between oxygen atoms not bonded to the same cation, a very reliable system of hydrogen bonds was obtained (Table 4 and Fig. 1). The valence balance (Table 5) for the various oxygen atoms is improved when the valence sums of bonds reaching these atoms are corrected for the contributions of the proposed hydrogen bonds. The hydrogen bond valence strengths were estimated by the procedure of DONNAY and ALLMANN (1970) from the distances between the hydrogen bonded atoms.

As it appears from Table 4 and Fig. 1 all the oxygen atoms are engaged in the hydrogen bonding system, apart from O(1), which is the common corner of three Cu octahedra and the sulphur tetrahedron, and O(3) hydroxyl group. Each of the three free corners of the sulphate group is acceptor in three hydrogen bonds. The water

Table 4. *Hydrogen bond system*: O···O *distances* (Å) *and bond valence contribution* (V.U.)

	O···O distance	Bond valence strength
O(8)—H···O(5)^{iv}	2.73	0.196
O(8)—H···O(6)^{ii}	2.79	0.171
O(9)—H···O(7)^{iv}	2.69	0.204
O(9)—H ···O(6)^{v}	2.95	0.116
···O(9)^{vi}	2.97	0.109
O(10)—H···O(6)^{ii}	2.73	0.195
O(10)—H···O(5)^{vii}	2.82	0.159
O(4)—H ···O(5)^{vii}	3.03	0.093
···O(7)^{iv}	3.05	0.090
O(2)—H···O(7)^{iv}	2.90	0.130

Table 5. *Bond valence balance* (V.U.), *calculated following* Donnay *and* Allmann (1970)

	Zn	Cu(1)	Cu(2)	S	Σc_V	$\Sigma c_V'$	
O(1)		0.148	0.062 0.104	1.527	1.841	1.841	O^{2-}
O(2)		0.217	0.510 0.491		1.218	1.088	OH^-
O(3)		0.373 0.397	0.420		1.190	1.190	OH^-
O(4)		0.442 0.423	0.413		1.278	1.095	OH^-
O(5)				1.473	1.473	1.921	O^{2-}
O(6)				1.512	1.512	1.984	O^{2-}
O(7)				1.488	1.488	1.912	O^{2-}
O(8)	0.333				0.333	−0.034	H_2O
O(9)	0.333				0.333	0.013	H_2O
O(10)	0.334				0.334	−0.018	H_2O

Σc_V: sum of the bond valences reaching the anion.

$\Sigma c_V'$: sum of the bond valences reaching the anion, after introduction of the hydrogen bond contribution.

molecules are donor in stronger bonds than those formed by the two hydroxyl oxygen atoms O(2) and O(4). The water molecule O(9) is engaged in a bifurcated hydrogen bond with a sulphate oxygen atom O(6) (2.95 Å) and a symmetry equivalent O(9) water molecule (2.97 Å). A second bifurcated bond is formed by O(4) hydroxyl anion with two sulphate oxygen atoms, O(5) and O(7), with bond distances 3.03 and 3.05 respectively.

Relationships with other minerals

As it was previously said, each Cu distorted octahedron shares six edges with six surrounding Cu octahedra to form a corrugated sheet parallel to (001), with crystalchemical formula $^{2}_{\infty}[(Cu,Zn)_2(OH)_3O]^-$. Closely similar corrugated sheets were found in serpierite (Sabelli and Zanazzi, 1968) and devillite (Sabelli and Zanazzi, 1971). As in ktenasite, also in serpierite and devillite sulphate tetrahedra are connected by corner sharing to both sides of the corrugated octahedral sheet, building up a composite tetrahedral-octahedral layer. The close

Table 6. *Unit cells* (Å and degrees) *and chemical formulae of mineral related to ktenasite*

						Chemical formula	*Z*
Ktenasite[1]	$a = 5.598$	$b = 6.121$	$c = 23.751$	$\beta = 95.55$	$P2_1/c$	$Zn_2(Cu,Zn)_8(SO_4)_4(OH)_{12} \cdot 12H_2O$	1
Serpierite[2]	$c = 21.853$	$b = 6.250$	$a = 22.186$	$\beta = 113.36$	$C2/c$	$Ca_2(Cu,Zn)_8(SO_4)_4(OH)_{12} \cdot 6H_2O$	4
Devillite[3]	$c = 22.191$	$b = 6.135$	$a = 20.870$	$\beta = 102.73$	$P2_1/c$	$Ca_2Cu_8(SO_4)_4(OH)_{12} \cdot 6H_2O$	4
Langite[4]	$b = 11.25$	$a = 6.05$	$c = 7.14$	$\alpha = 90.0$	Pb	$Cu_8(SO_4)_2(OH)_{12} \cdot 2H_2O$	1
Wroewolfeite[5]	$b = 5.65$	$a = 6.06$	$c = 14.36$	$\beta = 93.47$	$P2/c$ or Pc	$Cu_8(SO_4)_2(OH)_{12} \cdot 4H_2O$	1
Posnjakite[6]	$a = 10.578$	$b = 6.345$	$c = 7.863$	$\beta = 117.98$	Pa	$Cu_8(SO_4)_2(OH)_{12} \cdot 2H_2O$	1

[1] This paper.
[2] SABELLI and ZANAZZI (1968).
[3] SABELLI and ZANAZZI (1972).
[4] WAPPLER (1971).
[5] DUNN and ROUSE (1975).
[6] KOMKOV and NEFEDOV (1967), MELLINI and MERLINO (unpublished data).

similarity among the crystal structures of these minerals are reflected in the crystallographic and chemical data given in Table 6.

As in the case of serpierite and devillite, the layer structure found in ktenasite accounts very well for the habit of the crystals, which appear as plates flattened on {001}, for the good {001} cleavage and for the optical negative character of the mineral.

The main difference between ktenasite on one side and serpierite and devillite on the other side lies in the kind of connection between subsequent composite layers. In fact, whereas in ktenasite the zinc cations in the regular octahedral site coordinate six water molecules which are connected to the oxygen atoms of the sulphate group through hydrogen bonding, in serpierite and devillite the calcium atoms coordinate only three water molecules and complete their coordination with oxygen atoms of the sulphate groups, thus directly connecting subsequent composite layers. This explains the lower water content in these last minerals, together with the shorter value of d_{001} distance ($d_{001} = 20.36$ Å) in comparison with the value found in ktenasite ($d_{001} = 23.65$ Å).

A corrugated sheet similar to that present in ktenasite was also found in langite (Wappler, 1971). Sulphate groups are linked on one side of the sheet and no other cation is inserted between subsequent composite layers. The close relationships between the cell parameters of langite and wroewolfeite indicate that the minerals are very probably structurally similar. As regards posnjakite a reliable definition of its crystalchemical relations to the other minerals of the group should await the structure determination.

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