American Mineralogist, Volume 81, pages 244–248, 1996

Bechererite, $(Zn,Cu)_6Zn_2(OH)_{13}[(S,Si)(O,OH)_4]_2$, a novel mineral species from the Tonopah-Belmont mine, Arizona

GERALD GIESTER AND BRANKO RIECK

Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Althanstrasse 14, A-1090 Vienna, Austria

ABSTRACT

Bechererite is a new mineral found on dump material from the Tonopah-Belmont mine, Maricopa County, Arizona, U.S.A. It occurs as thin elongated crystals, commonly in hemispherical aggregates, and it is associated with rosasite, hydrozincite, willemite, smithsonite, paratacamite, and boleite. Bechererite is light green, transparent with vitreous luster, and has perfect cleavage parallel to {001}. It has a density of 3.45(5) g/cm³ and a Mohs hardness of 2–3. Optically, it is uniaxial (−) with $\epsilon = 1.611(1)$ and $\omega = 1.705(1)$. The empirical formula (based on 21 O atoms) is $(Zn_{4.93}Cu_{1.01})Zn_2(OH)_{13}(S_{1.10}Si_{0.95})[O_{5.30}(OH)_{2.70}]$, simplified to $(Zn,Cu)_6Zn_2(OH)_{13}[(S,Si)(O,OH)_4]_2$. The strongest lines in the X-ray powder diffraction pattern are [d_{obs} (Å)(I_{obs},hkl)] 7.37(100,001), 3.623(25,11$\bar{1}$), 3.282(30,012), 2.724(30,120), 2.556(50,121), and 1.572(20,410).

The crystal structure was solved by direct methods and refined to $R = 0.041$ on the basis of single-crystal X-ray diffraction data of 281 unique reflections up to $(\sin\theta)/\lambda = 0.48$ Å^{-1} [space group $P\bar{3}$, $a = 8.319(2)$, $c = 7.377(3)$ Å, $V = 442.1(1)$ Å^3, $Z = 1$]. The atomic arrangement of bechererite is characterized by sheets of edge-sharing octahedra with ordered vacancies, interconnected by Zn_2O_7 groups. Isolated XO_4 tetrahedra (X = S, Si) share a common corner with one O atom of the octahedral sheet. A complex system of hydrogen bonds occurs in bechererite.

INTRODUCTION

An unknown mineral was noticed in 1991 in a sample from dump material of the Tonopah-Belmont mine, Osborne Ag-Au district of Maricopa County, west-central Arizona. To date, samples from four vugs, each containing a few dozen crystals, have been recovered. The conspicuous habit of the mineral resembled spangolite, $Cu_6Al(SO_4)(OH)_{12}Cl \cdot 3H_2O$, but the distinctive color suggested that the mineral was new. Our studies confirmed that it is a copper zinc hydroxide sulfate silicate, closely related structurally to spangolite. The mineral is named for Karl Becherer, University of Vienna, who has contributed to the mineralogy of spangolite from the Lavrion deposit. The new mineral and the name were approved by the International Mineralogical Association Commission on New Minerals and Mineral Names. Type material is deposited in the collections of the Institut für Mineralogie und Kristallographie, University of Vienna, under catalog no. 8B\10–030#1, as well as at the Naturhistorisches Museum, Vienna, under catalog no. M 6789.

OCCURRENCE AND PARAGENESIS

The Tonopah-Belmont mine is hosted in a structurally isolated block of Miocene rocks that is in fault contact to the southeast with the Tertiary Belmont granite; on all other sides this block is surrounded by Proterozoic phyllite. The mineralization is controlled by a fault striking N75°E to N65°E, which is normal to a southwest-dipping low-angle fault, the major structure of the area. For a further account of the geology the reader is referred to Allen and Hunt (1988). The Tonopah-Belmont mine is a hydrothermal Au and Ag base metal vein deposit, and primary ore minerals are galena, chalcopyrite, sphalerite, gold, silver, and hematite. The alteration of these primary minerals yielded a suite of not less than 30 secondary minerals. Bechererite is associated with willemite and rosasite, which crystallized earlier, and hydrozincite as the latest mineral in this sequence. In one of the four vugs, the minerals smithsonite, paratacamite, and boleite were also found.

PHYSICAL PROPERTIES

Bechererite occurs as druses and hemispheres of trigonal acicular crystals with a maximum length of 250 μm along [001] and a diameter of 40 μm. The forms encountered (Fig. 1) are {001}, {120}, {241}, and {24$\bar{1}$}; no twinning was observed. The mineral is brittle and exhibits a well-developed cleavage parallel to (001). Measurement of Mohs hardness (2–3) and density [3.45(5) g/cm³] is inaccurate because of small crystal size. The density, calculated on the basis of the crystal chemistry and cell metrics, is 3.51 g/cm³. Bechererite is light green in plane-polarized light without visible pleochroism and has a white streak and vitreous luster. It is uniaxial negative, with ϵ

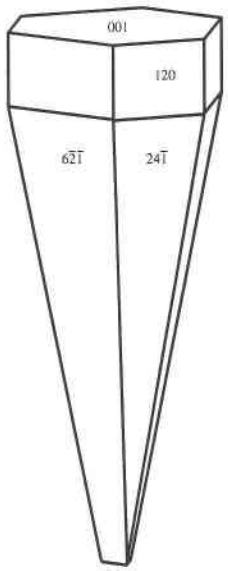

FIGURE 1. Idealized crystal drawing of bechererite.

= 1.611(1) and ω = 1.705(1). No dispersion was observed. Calculation of the Gladstone-Dale relationship using the constants of Mandarino (1981) yields a superior compatibility index. Bechererite is readily soluble in 1 *m* HCl.

CHEMISTRY

The chemical analysis was performed with an ARL-SEMQ electron microprobe. Operation conditions were 15 kV acceleration potential and about 15 nA sample current. Counting times for peak and background positions were 20 s and 2 × 10 s, respectively. Augite (Si), sphalerite (Zn, S), and chalcopyrite (Cu) were used as standards, and H_2O was calculated by difference because of the small quantities of material available. Five measurements yielded the mean composition (in weight percent): CuO 8.6 (6.6–10.4), ZnO 60.6 (57.9–63.9), SO_3 9.5 (9.0–10.1), SiO_2 6.1 (4.4–8.2), and 15.2 for H_2O (calculated to total 100 wt%). The empirical formula (formula basis = O_{21}) is $(Zn_{4.93}Cu_{1.01})Zn_2(OH)_{13}(S_{1.10}Si_{0.95})[O_{5.30}(OH)_{2.70}]$, suggesting $(Zn,Cu)_6Zn_2(OH)_{13}[(S,Si)(O,OH)_4]_2$. This formulation is confirmed by the crystal structure and with Zn:Cu = 7:1 and S:Si = 1:1.

X-RAY CRYSTALLOGRAPHY

Weissenberg photographs established that the mineral is trigonal with the possible space group $P3$ or $P\bar{3}$. A tiny crystal cluster was investigated using a Gandolfi camera, and from 52 lines (Table 1) the lattice parameters were refined to a = 8.322(1), c = 7.376(1) Å. Finally, a single crystal, 0.025 mm in diameter and 0.2 mm in length, was used for data collection on a Stoe AED2 four-circle diffractometer. The cell parameters, derived from 44 measured 2θ values, are a = 8.319(2), c = 7.377(3) Å, consistent within one standard deviation with the result of the Gandolfi measurement. Crystal data, details of the data collection, and the structure refinements are given in Table 2.

The X-ray intensities were corrected for Lorentz and polarization effects. The crystal structure was solved by direct methods in space group $P\bar{3}$ and refined to R = 0.041. Complex scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson 1992). Refined structural parameters, obtained by full-matrix least-squares techniques on F^2, are listed in Table 3. In the refinement in space group $P\bar{3}$ (52 variables), the X-atom position is statistically occupied by Si

TABLE 1. Powder diffraction data for bechererite

I_{obs}	d_{obs}	d_{calc}	*hkl*
100	7.37	7.38	001
5	5.15	5.15	101
10	4.158	4.161	110
10	3.690	3.688	002
25	3.623	3.624	11$\bar{1}$
30	3.282	3.283	012
3	3.238	3.238	021
10	2.757	2.760	112
30	2.724	2.724	120
5	2.576	2.577	202
50	2.556	2.555	121
2	2.403	2.402	300
1	2.328	2.327	103
1	2.284	2.284	301
15	2.191	2.191	122
1	2.116	2.117	113
1	2.081	2.081	220
0.5	2.030	2.031	023
3	2.014	2.013	302
0.5	1.998	1.999	130
1	1.928	1.929	131
5	1.843	1.844	004
10	1.826	1.825	123
5	1.811	1.812	222
1	1.784	1.787	104
7	1.756	1.757	312
3	1.618	1.619	042
20	1.572	1.573	410
1	1.550	1.551	133
7	1.5377	1.5381	411
10	1.5279	1.5270	12$\bar{4}$
5	1.5082	1.5087	232
1	1.4753	1.4752	005
3	1.4461	1.4467	412
5	1.3626	1.3620	240
7	1.3396	1.3394	24$\bar{1}$
1	1.3245	1.3249	413
5	1.2981	1.2982	33$\bar{2}$
3	1.2777	1.2777	24$\bar{2}$
1	1.2220	1.2214	51$\bar{2}$
1	1.1965	1.1966	414
1	1.1916	1.1914	24$\bar{3}$
1	1.1284	1.1280	43$\bar{2}$
5	1.0958	1.0956	244
1	1.0758	1.0759	415
0.5	1.0533	1.0533	16$\bar{2}$
2	1.0297	1.0296	700
3	1.0199	1.0197	071
2	0.9915	0.9917	532
3	0.9497	0.9497	073
2	0.9078	0.9080	360
5	0.8989	0.8990	704

Note: Intensities visually estimated. Gandolfi camera (d = 114.6 mm), Cu$K\alpha$ radiation, Ni filter, NBS*AIDS83 (Mighell et al. 1981) for refinement of the lattice parameters from 52 reflections (indexed from calculated pattern): a = 8.322(1), c = 7.376(1) Å.

TABLE 2. Summary of crystal data, X-ray measurements, and structure refinements

Bechererite	$(Zn,Cu)_6Zn_2(OH)_{13}$-$[(S,Si)(O,OH)_4]_2$
Space group	$P\bar{3}$
a (Å)	8.319(2)
c (Å)	7.377(3)
V (Å^3)	442.1
Z	1
ρ_{calc} (g/cm^3)	3.51
μ(Mo$K\alpha$) (cm^{-1})	108
(sin θ)/λ_{max} (Å^{-1})	0.48
$hkl_{min,max}$	−8,8; −8,8; 0,7
Refl. measured	913
Unique refl.	281
Refl. with $F_o > 4\sigma_{F_o}$	212
2θ range for lattice parameters (°)	26–32
Variable parameters	57
$R1$, $R2_w$	0.041, 0.088
$R1 = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	
$R2_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$	
$w = 1/[\sigma^2(F_o^2) + (0.053P)^2]$	
$P = \{[\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2\}/3$	

Note: Stoe AED2 four-circle diffractometer, Mo$K\alpha$ radiation, graphite monochromator; 2θ-ω scans, 40 steps/reflection, increased for α_1-α_2 dispersion, 2 × 6 steps for background correction, 0.03° and 1.0–4.0 s/step, three standard reflections every 120 min. SHELXL-93 (Sheldrick 1993) for structure refinement.

and S, with an averaged geometry. An ordering of Si and S on two distinct positions would be possible in $P3$. Because of the small size of the crystal, only 281 unique reflections, 212 of them with $F_o > 4\sigma_{Fo}$, could be measured. A refinement in the acentric space group $P3$ (with isotropic displacement factors to reduce the number of parameters) resulted in standard deviations of the relevant interatomic distances, which were much too high to allow any proof of ordering. Therefore, we restricted our description of bechererite to the centrosymmetric model; yet, upon availability of new data, a revision of the space group might be necessary.

The approximate positions of most H atoms were derived on the basis of the stereochemistry. Some were also located by a difference-Fourier map and could be refined by restricting the O-H distances to 0.85(5) Å. Final residual electron densities were <0.6 e/Å^3. Selected interatomic bond distances and angles are given in Table 4.

TABLE 4. Interatomic bond lengths (Å) and bond angles (°) in bechererite

M1-O5	2.018(9)
M1-O5[a]	2.042(9)
M1-O5[b]	2.074(9)
M1-O4[c]	2.114(9)
M1-O4	2.152(8)
M1-O1[d]	2.329(10)
⟨M1-O⟩	⟨2.122⟩
M2-O3	1.883(3)
M2-O4[e,f] × 3	1.936(9)
⟨M2-O⟩	⟨1.923⟩
O4-M2-O4 × 3	111.0(3)
O4-M2-O3 × 3	107.9(2)
X-O1	1.608(18)
X-O2[g,h] × 3	1.554(9)
⟨X-O⟩	⟨1.568⟩
O2-X-O2 × 3	108.4(4)
O2-X-O1 × 3	110.6(4)

Note: equivalent positions: a = $x - y, x, -z$; b = $1 - x + y, 1 - y, z$; c = $y, y - x, -z$; d = $1 - x, 1 - y, -z$; e = $-y, x - y, z$; f = $y - x, -x, z$; g = $y - x, 1 - x, z$; h = $1 - y, 1 + x - y, z$.

Observed and calculated structure factors are given in Table 5.[1]

DISCUSSION

Description of the crystal structure

The structural arrangement of bechererite, $M1_6M2_2(OH)_{13}[X(O,OH)_4]_2$, is characterized by brucite-like sheets of edge-sharing $M1O_6$ octahedra parallel to (001) but with the site position 1a (0,0,0) vacant (Fig. 2). These sheets are interconnected by $M2_2O_7$ groups. In addition, XO_4 tetrahedra (X = S, Si) are attached to the sheets (Fig. 3) and take part in the linkage of the sheets by hydrogen bonding.

The M1 position, occupied by Zn and Cu (Zn/Cu ≈ 5/1), is octahedrally coordinated (distorted octahedron, 3 × O3, 2 × O4, 1 × O1). The M1-O distances range from

[1] A copy of Table 5 may be ordered as Document AM-96-602 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 3. Atomic coordinates and displacement parameters for bechererite

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M1	0.4199(2)	0.2853(2)	−0.0005(2)	0.019(1)	0.014(1)	0.027(1)	−0.000(7)	−0.002(1)	0.009(1)	0.020(1)
M2	0	0	0.2447(4)	0.020(1)	0.020(1)	0.019(2)	0	0	0.010(1)	0.020(1)
X	⅓	⅔	0.4039(9)	0.035(3)	0.035(3)	0.033(4)	0	0	0.017(1)	0.034(2)
O1	⅓	⅔	0.186(2)	0.033(7)	0.033(7)	0.042(11)	0	0	0.016(3)	0.036(5)
O2	0.328(1)	0.489(1)	0.478(1)	0.065(7)	0.029(6)	0.029(6)	−0.001(5)	−0.003(6)	0.034(6)	0.036(3)
O3	0	0	½	0.149(24)	0.149(24)	0.008(19)	0	0	0.074(12)	0.102(15)
O4	0.189(1)	0.244(1)	0.164(1)	0.025(6)	0.030(6)	0.018(5)	−0.007(5)	−0.004(5)	0.012(5)	0.025(3)
O5	0.478(1)	0.104(1)	0.124(1)	0.021(6)	0.015(5)	0.022(5)	0.001(5)	0.005(5)	0.005(5)	0.021(3)
H1	0.35(3)	0.39(2)	0.48(3)							
H2	0.23(1)	0.32(1)	0.26(1)							
H3	0.45(2)	0.10(2)	0.24(1)							

Note: The anisotropic displacement factor is defined as $\exp(-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_ja^*_ia^*_j)$. The atomic positions M1 (Zn:Cu ≈ 5:1) and X (Si:S ≈ 1:1) are statistically occupied. The atom position of H1 is one-half occupied.

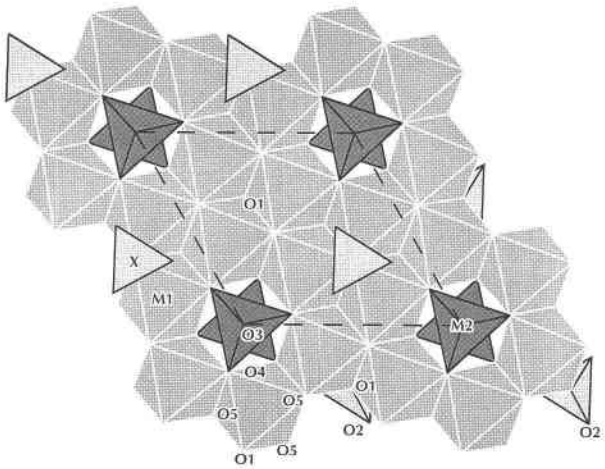

FIGURE 2. The crystal structure of bechererite projected onto (001). The drawing was made with ATOMS 2.3 (Dowty 1993).

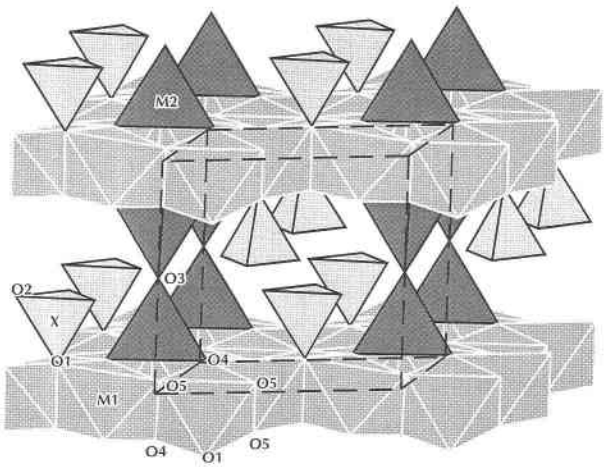

FIGURE 3. Perspective view of the atomic arrangement of bechererite.

2.018 to 2.329 Å, and the nonopposite O-M1-O angles range from 81.1(4) to 98.7(4)°. These octahedra are linked to each other by five common edges to form the sheet.

The M2 atom (essentially Zn) is tetrahedrally coordinated to three O4 atoms and one O3 atom, the latter of which cornerlinks two ZnO_4 tetrahedra to a Zn_2O_7 group. The mean Zn-O distance of 1.923 Å is rather short; the Zn-O3-Zn angle is formally 180°, but the highly anisotropic displacement parameters of the bridging O3 atom clearly indicate some kind of disorder (static or dynamic), with local violation of the symmetry $\bar{3}$. The real Zn-O3 distances are therefore larger, as analogously reported for compounds with symmetry-restricted X_2O_7 ($X = As^{5+}$, Si^{4+}) groups forcing straight X-O-X bonds (cf. Liebau 1985; Effenberger and Pertlik 1993). Corner-linked ZnO_4 tetrahedra as subunits of sheet or framework structures are well known [e.g., in clinohedrite, $CaZnSiO_4 \cdot H_2O$ (Venetopoulos and Rentzeperis 1976); hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$ (Hill and Jones 1976); phosphophyllite, $Zn_2Fe(PO_4)_2 \cdot 4H_2O$ (Hill 1977); and many others]. Distinct Zn_2O_7 groups are less common; an example is $KZn_2H(PO_4)_2$ (Averbuch-Pouchot 1979), though Zn-O-Zn is not linear and the bridging O atom is bonded to other ions.

As determined from the interatomic distances, the tetrahedral X position is occupied by Si and S, approximately 1/2 each. The mean X-O bond length is 1.568 Å, between 1.47 and 1.62 Å, known for SO_4 and SiO_4 tetrahedra, respectively. The tetrahedron, bound by O1 to the octahedral sheet, is further linked by hydrogen bonds of the three O2 atoms. The vibrational ellipsoids of O1, X, and especially O2 are somewhat large because of the mixed occupancy of the $X(O,OH)_4$ tetrahedron.

The O1 atom is coordinated with a distorted tetrahedral environment to three M1 atoms of one octahedral sheet and one adjacent X atom and is therefore excluded as a donator atom of an OH group. O2 belongs to the XO_4 tetrahedron and is further involved in the hydrogen-bonding system. As already pointed out, O3 is bonded to two Zn2 atoms with the rather short distance of 1.883 Å. This atom is probably statistically shifted from position 1*b* (0,0,½), resulting in greater Zn2-O3 distances and a more realistic Zn2-O3-Zn2 geometry. The position of the respective H atom could not be located, but on the basis of bond-valence calculations, O3 is undoubtedly the O atom of an OH group. For O4 and O5, the atomic coordinates of the respective H atoms (H2 and H3) were approximately determined, resulting in both cases in a tetrahedral arrangement with three additional M ligands ($2 \times M1 + 1 \times M2$ for O4; $3 \times M1$ for O5).

Bond-valence calculations (Brese and O'Keeffe 1991), excluding contributions of H atoms, yield bond strengths (in valence units) of 1.21, 1.23, 1.16, and 1.20 for O2, O3, O4, and O5, respectively, clearly indicating that these atoms belong to OH groups. The calculation for the O1 atom, which is tetrahedrally coordinated by three M and one X atom, gives 1.60 vu. This value undoubtedly is unsatisfactory, but one has to consider that the X-O1 bond length is rather inaccurate and averaged because of the statistical occupancy of X by S or Si. To obtain a bond strength of 2 vu, the X-O1 distance must be about 1.5 Å, which is approximately within six standard deviations of the X-O1 bond length. Excluding O-O edges within coordination polyhedra, the hydrogen-bonding scheme is derived as follows: O3 (strictly on site 1*b*) is isolated, with nearest O contacts of six O2 atoms as far as 3.594 Å. This distance is reduced by the obvious disorder of O3, which leads to a shift toward O2. O4 and O5 form H bonds O4-H2···O2 and O5-H3···O2 with O-O distances of 2.915 and 2.968 Å, respectively. For a balance of charges, approximately 50% of the three O2 ligands of the $X(O,OH)_4$ tetrahedra would have to be OH groups (O2-H1) with rather short O2-O2 contacts (2.794 Å) favoring hydrogen bonding O2-H1···O2. In space group *P*3 (by an ordering of the SO_4 and SiO_4 groups only) a differentiation in short X-O and long X-OH dis-

tances might become possible, but without overcoming the general problem of the quite unusual hydrogen bonding.

Related crystal structures

Sheets formed of full or partial hydrated octahedra that share common edges [analogous to brucite, $Mg(OH)_2$] are quite common building units in minerals and synthetic compounds. Some of them have empty cavities within the sheets as found in bechererite (1/7 of the octahedral positions are vacant), e.g., 1/4 in $Zn_5(OH)_6Cl_2 \cdot H_2O$ (Allman 1968), 2/9 in lawsonbauerite [$(Mn,Mg)_9Zn_4(SO_4)_2(OH)_{22} \cdot 8H_2O$, Treiman and Peacor 1982], and 2/11 in mooreite [$(Mg,Zn,Mn)_{15}(SO_4)_2(OH)_{26} \cdot 8H_2O$, Hill 1980] with Zn tetrahedra above and below the sheet having common faces with the vacant sites. In spangolite, $Cu_6Al(SO_4)(OH)_{12}Cl \cdot 3H_2O$ (Merlino et al. 1992; Hawthorne et al. 1993), the analogous position, which is vacant in bechererite, is occupied by Al.

XO_4 tetrahedra linked by one corner with a brucite-like sheet are a well-known structural feature. In spangolite, langite [$Cu_4(OH)_6SO_4 \cdot 2H_2O$, Gentsch and Weber 1984], wroewolfeite [$Cu_4(OH)_6SO_4 \cdot 2H_2O$, Hawthorne and Groat 1985], and posnjakite [$Cu_4(OH)_6SO_4 \cdot H_2O$, Mellini and Merlino 1979], the SO_4 groups are attached to only one side of the sheet. In ktenasite [$Zn_2(Cu,Zn)_8(OH)_{12}(SO_4)_4 \cdot 12H_2O$, Mellini and Merlino 1978], campigliaite [$Cu_4Mn(OH)_6(SO_4)_2 \cdot 4H_2O$, Menchetti and Sabelli 1982], serpierite [$Ca_2(Cu,Zn)_8(OH)_{12}(SO_4)_4 \cdot 6H_2O$, Sabelli and Zanazzi 1968], and devillite [$Ca_2Cu_8(OH)_{12}(SO_4)_4 \cdot 6H_2O$, Sabelli and Zanazzi 1972], the groups are attached to both sides.

The single layers are interconnected by hydrogen bonds between only $\pm H_2O$, OH, and SO_4 groups of opposite sheets (langite, wroewolfeite, spangolite, posnjakite) or by hydrogen bonding with interlayering of additional polyhedra [$M(OH,H_2O)_6$ octahedra] as in campigliaite, devillite, and serpierite.

Chalcophanite, $ZnMn_3O_7 \cdot 3H_2O$ (Post and Appleman 1988), forms sheets of edge-sharing $Mn^{4+}O_6$ octahedra, with 1/7 of them vacant and ordered; but unlike bechererite, the Zn ions, situated above and below the vacancies, are sixfold coordinated, forming $Zn[O_3(H_2O)_3]$ octahedra.

Acknowledgments

The authors are grateful to P. Hubert and K. Schebesta, Vienna, for providing the samples. Chemical analyses were kindly performed by E. Libowitzky (EDX) and F. Brandstätter. Partial financial support was provided by the JCPDS/ICDD under grant-in-aid 90–03. The authors thank E. Tillmanns, J. Zemann, and W. Kiesl for helpful discussions.

References cited

Allen, F., and Hunt, W. (1988) The Tonopah-Belmont mine, Maricopa County, Arizona. Mineralogical Record, 19, 139–143.

Allman, R. (1968) Verfeinerung der Struktur des Zinkhydroxidchlorids: II. $Zn_5(OH)_8Cl_2 \cdot H_2O$. Zeitschrift für Kristallographie, 126, 417–426.

Averbuch-Pouchot, M.T. (1979) Structure du Monophosphate Acide de Potassium-Zinc: $KZn_2H(PO_4)_2$. Acta Crystallographica, B35, 1452–1454.

Brese, N.E., and O'Keeffe, M. (1991) Bond-valence parameters for solids. Acta Crystallographica, B47, 192–197.

Dowty, E. (1993) ATOMS 2.3: A computer program for displaying atomic structures. Shape Software, Kingsport, Tennessee.

Effenberger, H., and Pertlik, F. (1993) Crystal structures of $Ag_5Cu(AsO_4)(As_2O_7)$ and $Ag_7Cu(As_2O_7)Cl$ with a survey on pyroarsenate anions. Zeitschrift für Kristallographie, 207, 223–236.

Gentsch, M., and Weber, K. (1984) Structure of langite, $Cu_4[(OH)_6|SO_4] \cdot 2H_2O$. Acta Crystallographica, C40, 1309–1311.

Hawthorne, F.C., and Groat, L.A. (1985) The crystal structure of wroewolfeite, a mineral with $[Cu_4(OH)_6(SO_4)(H_2O)]$ sheets. American Mineralogist, 70, 1050–1055.

Hawthorne, F.C., Kimata, M., and Eby, R.K. (1993) The crystal structure of spangolite, a complex copper sulfate sheet mineral. American Mineralogist, 78, 649–652.

Hill, R.J. (1977) The crystal structure of phosphophyllite. American Mineralogist, 62, 812–817.

——— (1980) The structure of mooreite. Acta Crystallographica, B36, 1304–1311.

Hill, R.J., and Jones, J.B. (1976) The crystal structure of hopeite. American Mineralogist, 61, 987–995.

Liebau, F. (1985) Structural chemistry of silicates: Structure, bonding, and classification, 347 p. Springer-Verlag, Berlin.

Mandarino, J.A. (1981) The Gladstone-Dale relationship: IV. The compatibility concept and its application. Canadian Mineralogist, 70, 441–450.

Mellini, M., and Merlino, S. (1978) Ktenasite, another mineral with $^2_\infty[(Cu,Zn)_2(OH)_3O]^-$ octahedral sheets. Zeitschrift für Kristallographie, 147, 129–140.

——— (1979) Posnjakite: $^2_\infty[Cu_4(OH)_6(H_2O)O]$ octahedral sheets in its structure. Zeitschrift für Kristallographie, 149, 249–257.

Menchetti, S., and Sabelli, C. (1982) Campigliaite, $Cu_4Mn(SO_4)_2(OH)_6 \cdot 4H_2O$, a new mineral from Campiglia Marittima, Tuscany, Italy. American Mineralogist, 67, 385–393.

Merlino S., Pasero, M., Sabelli, C., and Trosti-Ferroni, R. (1992) Crystal structure refinement of spangolite, a hydrated basic sulfate of copper and aluminum, from three different occurrences. Neues Jahrbuch für Mineralogie Monatshefte, 349–357.

Mighell, A.D., Hubbard, C.R., and Stalick, J.K. (1981) NBS*AIDS83. A FORTRAN program for crystallographic data evaluation. NBS Technical Note 1141.

Post, J.E., and Appleman, D.E. (1988) Chalcophanite, $ZnMn_3O_7 \cdot 3H_2O$: New crystal-structure determinations. American Mineralogist, 73, 1401–1404.

Sabelli, C., and Zanazzi, P.F. (1968) The crystal structure of serpierite. Acta Crystallographica, B24, 1214–1221.

——— (1972) The crystal structure of devillite. Acta Crystallographica, B28, 1182–1189.

Sheldrick, G.M. (1993) SHELXL-93 program for crystal structure refinement. University of Göttingen, Germany.

Treiman, A.H., and Peacor, D.R. (1982) The crystal structure of lawsonbauerite, $(Mn,Mg)_9Zn_4(SO_4)_2(OH)_{22} \cdot 8H_2O$, and its relation to mooreite. American Mineralogist, 67, 1029–1034.

Venetopoulos, C.C., and Rentzeperis, P.J. (1976) Redetermination of the crystal structure of clinohedrite, $CaZnSiO_4 \cdot H_2O$. Zeitschrift für Kristallographie, 144, 377–392.

Wilson, A.J.C., Ed. (1992) International tables for crystallography, vol. C, 883 p. Kluwer Academic, Dordrecht, the Netherlands.

Manuscript received January 30, 1995
Manuscript accepted August 15, 1995