

SIMONKOLLEITE, $\text{Zn}_5(\text{OH})_8\text{Cl}_2(\text{H}_2\text{O})$, A DECORATED INTERRUPTED-SHEET STRUCTURE OF THE FORM $[\text{M}\phi_2]_4$

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ABSTRACT

The crystal structure of simonkolleite, $\text{Zn}_5(\text{OH})_8\text{Cl}_2(\text{H}_2\text{O})$, rhombohedral, space group $R\bar{3}m$, a 6.3412(3), c 23.646(1) Å, V 823.4(1) Å³, $Z = 3$, has been refined to an R index of 1.6% based on 284 observed (5σ) reflections measured with $\text{MoK}\alpha$ X-radiation. There are two distinct Zn sites fully occupied by Zn: Zn(1) is octahedrally coordinated by six (OH) groups, $\langle \text{Zn}(1)-\text{OH} \rangle = 2.127$ Å, and Zn(2) is tetrahedrally coordinated by three (OH) groups and one Cl atom, $\langle \text{Zn}(2)-\text{OH}, \text{Cl} \rangle = 2.041$ Å. The $(\text{Zn}\phi_6)$ octahedra (ϕ : O, OH, Cl) form an edge-sharing dioctahedral sheet similar to that observed in dioctahedral micas. On each side of the vacant octahedron, a $(\text{Zn}\phi_4)$ tetrahedron is attached to three anions of the sheet and points away from the sheet. The decorated sheet can be written as $[\text{M}_3(\text{T}\phi_4)_2\phi_2]$, where $\text{M} = [^{60}\text{Zn}]$, $\text{T} = [^{14}\text{Zn}]$ and $\phi = \text{OH}, \text{Cl}$. Intercalated between adjacent sheets are interstitial (H_2O) groups. The sheets are held together by hydrogen bonding from (OH) groups of one sheet to Cl anions of adjacent sheets, and to interstitial (H_2O) groups. Simonkolleite can be considered as a decorated sheet structure of the form $[\text{M}\phi_2]_4$ with an interrupted sheet, and is related to the structures of ciangiulite, gordaite, namuwite, bechererite, chalcophyllite, ramsbeckite, chalcophanite and claringbullite.

Keywords: simonkolleite, crystal structure.

SOMMAIRE

Nous avons affiné la structure cristalline de la simonkolleite, $\text{Zn}_5(\text{OH})_8\text{Cl}_2(\text{H}_2\text{O})$, rhomboédrique, groupe spatial $R\bar{3}m$, a 6.3412(3), c 23.646(1) Å, V 823.4(1) Å³, $Z = 3$, jusqu'à un résidu R de 1.6% en utilisant 284 réflexions observées (5σ) mesurées avec rayonnement $\text{MoK}\alpha$. La structure contient deux sites Zn distincts, qu'occupent le Zn. Le site Zn(1) montre une coordinence octaédrique avec six groupes (OH), $\langle \text{Zn}(1)-\text{OH} \rangle = 2.127$ Å, et le site Zn(2) possède une coordinence tétraédrique, impliquant trois groupes (OH) et un atome Cl, $\langle \text{Zn}(2)-\text{OH}, \text{Cl} \rangle = 2.041$ Å. L'octaèdre $(\text{Zn}\phi_6)$ (ϕ : O, OH, Cl) définit un feuillet dioctaédrique par partage d'arêtes, tout comme dans les micas dioctaédriques. De chaque côté de l'octaèdre manquant, un tétraèdre $(\text{Zn}\phi_4)$ est rattaché aux trois anions du feuillet, avec le sommet du tétraèdre orienté dans la direction opposée. On peut écrire ainsi la stoechiométrie du feuillet ainsi décoré: $[\text{M}_3(\text{T}\phi_4)_2\phi_2]$, dans laquelle l'expression $\text{M} = [^{60}\text{Zn}]$, $\text{T} = [^{14}\text{Zn}]$ and $\phi = \text{OH}, \text{Cl}$. Des groupes interstitiels de H_2O sont intercalés entre les feuillets. Des liaisons hydrogène entre groupes (OH) d'un feuillet aux anions Cl des feuillets adjacents, et aux groupes (H_2O) interstitiels, rattachent le tout. La structure en feuillets décorés de la simonkolleite aurait la forme $[\text{M}\phi_2]_4$, avec interruption dans les feuillets. Elle a des points communs avec les structures de ciangiulite, gordaite, namuwite, bechererite, chalcophyllite, ramsbeckite, chalcophanite et claringbullite.

Mots-clés: simonkolleite, structure cristalline.

INTRODUCTION

Simonkolleite was described as a new mineral by Schmetzer *et al.* (1985). It occurs as a product of weathering of zinc-bearing slags at Richelsdorf, Germany, and is associated with native zinc, hydrocerussite, diaboite, zincite and hydrozincite. Simonkolleite is colorless, forms tabular hexagonal crystals up to 1 mm in diameter, and has perfect cleavage parallel to (001). The crys-

tal structure of the synthetic analogue of simonkolleite was reported by Nowacki & Silverman (1961) and Allmann (1968). As part of our continuing interest in hydroxy-hydrated Cu-Zn oxysalts (Hawthorne 1985, Hawthorne & Groat 1985, Eby & Hawthorne 1989a, b, 1990, 1993, Burns *et al.* 1995, Hawthorne & Schindler 2000), we have refined the crystal structure of simonkolleite and present the results here.

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EXPERIMENTAL

The crystals used in this work are from the type locality and were obtained from Mr. Forrest Cureton. A small crystal measuring $25 \times 80 \times 100 \mu\text{m}$ was attached to a glass fiber and mounted on a Bruker *P4* automated four-circle diffractometer equipped with SMART 1K CCD detector and MoK α X-radiation. A total of 4699 reflections over the range $3 \leq 2\theta \leq 60^\circ$ was collected according to the procedure described by Cooper & Hawthorne (2001), using 0.2° framewidths and 90 s frames; this total is well in excess of the number of reflections in the Ewald sphere, and afforded considerable redundancy. The unit-cell dimensions (Table 1) were refined by least-squares using the positions of 2940 reflections with $I > 10 \sigma I$. The data were corrected for absorption by SADABS, reducing $R(\text{int})$ from 6.5 to 2.9%. Reflections were corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors; of the 340 unique reflections, 284 reflections were considered as observed [$|F_o| \geq 5\sigma F$].

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms were taken from the International Tables for Crystallography (1992). R

TABLE 1. MISCELLANEOUS INFORMATION FOR SIMONKOLLEITE			
<i>a</i> (Å)	6.3412(3)	crystal size (mm)	0.025 x 0.080 x 0.100
<i>c</i>	23.646(1)	radiation	MoK α
<i>V</i> (Å ³)	823.4(1)	No. of reflections	4699
Sp. Gr.	<i>R</i> $\bar{3}m$	No. in Ewald sphere	2824
<i>Z</i>	3	No. unique reflections	340
<i>D</i> _{meas} * (g/cm ³)	3.2	No. <i>F</i> _o > 5 σ <i>F</i>	284
<i>D</i> _{calc} (g/cm ³)	3.34	<i>R</i> (merge) %	1.6
		<i>R</i> (obs) %	1.6
		<i>wR</i> (<i>F</i> ²) %	1.6
Cell content	3 {Zn ₆ (OH) ₆ Cl ₂ (H ₂ O)}		
$R = \sum F_o - F_c / \sum F_o $			
$wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/4}, w = 1/\sigma^2 F_o \cdot [1 - \exp(-1.1 \{\sin\theta/\lambda\}^2)]$			

* from Schmetzer *et al.* (1985)

TABLE 2. ATOM POSITIONS AND DISPLACEMENT FACTORS FOR SIMONKOLLEITE

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂	<i>U</i> _{eq}
Zn(1)	1/2	0	0	0.0099(2)	0.0085(2)	0.0177(2)	0.0004(1)	0.0002(1)	0.0042(1)	0.0122(1)
Zn(2)	0	0	0.07172(2)	0.0114(2)	0.0114(2)	0.0145(2)	0	0	0.0057(1)	0.0124(1)
Cl	0	0	0.16948(5)	0.0311(4)	0.0311(4)	0.0137(4)	0	0	0.0156(2)	0.0253(3)
O(1)	0.8288(2)	0.1712(2)	0.04988(7)	0.0128(5)	0.0128(5)	0.0133(7)	0.0003(3)	-0.0003(3)	0.0073(6)	0.0125(5)
O(2)	0	0	0.3741(1)	0.0117(7)	0.0117(7)	0.0115(13)	0	0	0.0059(4)	0.0117(6)
O(3) [§]	0.969(1)	0.031(1)	0.502(3)							0.0369(49)
H(1)	0.786(4)	0.214(4)	0.086(1)							0.0500 *
H(2)	0	0	0.4155(1)							0.0500 *

[§] O(3) is an (H₂O) group with a site occupancy of 1/6. * constrained in refinement.

indices are of the form given in Table 1, and are expressed as percentages. The Bruker SHELXTL PLUS (PC version) system of programs was used for this work.

Refinement was initiated with the positional parameters reported for the synthetic analogue by Allmann (1968). The structure refined rapidly to an *R* index of ~2% for a model with anisotropic-displacement parameters for all non-H atoms. At this stage, the H sites were found on a difference-Fourier map and input into the refinement with the soft constraint that O–H distances are ~0.98 Å. Full-matrix least-squares refinement converged to an *R* index of 1.6%. Final positional and displacement parameters are given in Table 2, and selected interatomic distances and angles are listed in Table 3. Observed and calculated structure-factors are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION OF THE STRUCTURE

Coordination of the cations

There are two crystallographically distinct Zn sites in simonkolleite, both of which are fully occupied by Zn. The Zn(1) site is coordinated by six (OH) groups in an octahedral arrangement with a $\langle \text{Zn}-(\text{OH}) \rangle$ distance of 2.127 Å. The Zn(2) site is coordinated by three (OH) groups, and one Cl atom in a tetrahedral arrangement, with a $\langle \text{Zn}-(\text{OH}), \text{Cl} \rangle$ distance of 2.041 Å. The Zn(1) octahedron has four long equatorial bonds and two short apical bonds. As discussed in detail by Burns & Hawthorne (1995), octahedrally coordinated Cu²⁺ shows elongation (rather than shortening) of apical bonds, and hence one does not expect an isostructural Cu²⁺ analogue of simonkolleite. This apical shortening of the Zn(1) octahedron in simonkolleite is a result of the bond-valence requirements of the coordinating (OH) groups and the connectivity of polyhedra in the structure. The equatorial (OH) groups [= O(1)] are coordinated by two Zn(1) cations and one Zn(2) cation, whereas the apical (OH) groups [= O(2)] are coordinated

by three Zn(1) cations. As Zn(1) is [6]-coordinated and Zn(2) is [4]-coordinated, the local bond-valence requirements (Table 4) require the Zn(1)–O(1) bonds to be considerably longer than the Zn(1)–O(2) bonds. The Zn(2) tetrahedron has three short Zn(2)–O(1) bonds and one long Zn(2)–Cl bond. This is the only cation–Cl bond, and hence Cl must be an acceptor anion for several hydrogen bonds in order to satisfy its bond-valence requirements.

Hydrogen bonding

The bond-valence incident at the various anions from the Zn cations (Table 4) show O(1) and O(2) to be (OH) groups and O(3) to be an (H₂O) group. The H atoms associated with the (OH) groups were located in the refinement (Table 2), and a reasonable hydrogen-bonding arrangement is apparent (Tables 3, 4). The H(1) atom hydrogen-bonds to a Cl anion of the adjacent layer with an H...Cl distance of 2.256 Å, and each Cl atom is an acceptor of three hydrogen bonds from H(1) atoms of the adjacent layer (Fig. 1). The H(2) atom hydrogen-

bonds to the O(3) anion, an interstitial (H₂O) group. Each O(3) anion [= (H₂O) group] is an acceptor of two hydrogen bonds from the adjacent sheets (Fig. 1).

The bond-valence incident at O(3) (Table 4) shows it to be an (H₂O) group, as it does not bond directly to any cation in the structure. The associated H atoms of the (H₂O) group were not found in the final difference-Fourier map. This is not unexpected, as the O(3) anion ideally lies on Wyckoff position 3b with point symmetry $\bar{3}m$, and the (H₂O) group cannot conform to this point symmetry as its maximal point-symmetry, is $mm2$. Even though O(3) is disordered off the 3b position to the 18h position, the H atoms of the group *must* be disordered to conform with the long-range symmetry $R\bar{3}m$, and hence we do not expect to be able to locate these H atoms by X-ray diffraction. However, there are two H (equivalent) atoms associated with O(3), and the ratio of (H₂O):Cl is 1:2; thus, each Cl anion will receive one hydrogen bond from an (H₂O) group. Hence Cl is an acceptor of four hydrogen bonds (Table 4).

Structure topology

Each (Zn ϕ_6) octahedron (ϕ : unspecified ligand) shares four edges with adjacent octahedra to form a dioctahedral sheet similar to that in muscovite and other dioctahedral phyllosilicates. In this sheet, each vacant octahedron is sandwiched between two (Zn ϕ_4) tetrahedra with their apices pointing away from the sheet. The resulting sheet is of the form $[M_3(T\phi_4)_2\phi_2]$ or $[^{16}Zn_3\{Zn(OH)_3Cl\}_2(OH)_2]$ (Fig. 2). Because of the rhombohedral symmetry, adjacent sheets are shifted such that the rows of projecting $\{Zn(OH)_3Cl\}$ tetrahedra intermesh (Fig. 3) and intercalate parallel rows of (H₂O) groups.

RELATED STRUCTURES

Hawthorne & Schindler (2000) examined the principles involved in the structures of hydroxy-hydrated copper (and zinc) minerals based on decorated $[Cu^{2+}\phi_2]_N$ sheets. The structure of simonkolleite fits into this scheme if we write the formula in the following way: $[^{16}Zn_3\{^{14}Zn(OH)_3Cl\}_2(OH)_2](H_2O)$. First, we include the vacant octahedra into the formula: $[^{16}Zn_3\Box]$. Next, we see from Figure 2 that each tetrahedron links to three octahedral ligands, and hence we can write each $\{Zn(OH)_3Cl\}$ tetrahedron as ϕ_3 (ϕ : any anion of the sheet). Hence the above formula reduces to $[(Zn_3\Box)\phi_{6+2}] = [M_4\phi_8] = [M\phi_2]_4$ where $M = [^{16}(Zn, \Box)]$ and ϕ = octahedron ligands. Thus simonkolleite has a structure based on a decorated $(^{16}M\phi_2)_N$ sheet.

Hawthorne & Schindler (2000) discussed the structures that fall into this category of decorated $[M\phi_2]_N$ sheets. Of particular interest in the present case are those structures in which there are vacancies at some of the octahedrally coordinated sites in the sheet, the "interrupted" sheets; these are listed in Table 5. The nature of

Zn(1)–O(1)	x4	2.157(1)	Zn(2)–O(1)b	x3	1.950
Zn(1)–O(2)a	x2	2.068(1)	Zn(2)–Cl		2.312
<Zn(1)–O>		2.127			
O(1)–H(1)		0.98(2)	O(2)–H(2)		0.980(4)
H(1)–Clc		2.26(2)	H(2)–O(3)b		2.07(6)
O(1)–H(1)...Clc		173(1)	H(2)–O(3)d	x2	1.99(6)
			O(2)–H(2)–O(3)b		170.4(1)
			O(2)–H(2)–O(3)d	x2	170.1(3)

a: $1/3+x$, $2/3+y-1$, $2/3+z-1$; b: $-1+x$, y , z ; c: $2/3+y$, $1/3+x$, $1/3-z$; d: $1-x$, $-y$, $1-z$.

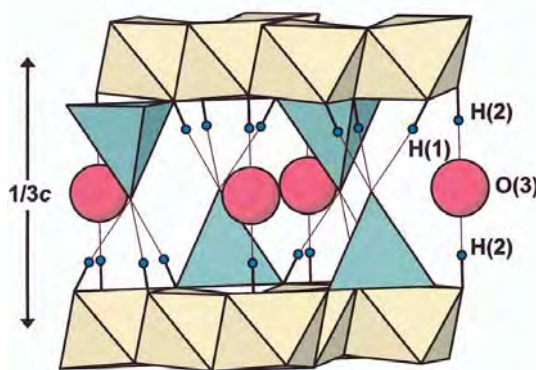


FIG. 1. The hydrogen bonding arrangement of the (OH) groups in simonkolleite; Zn(1) octahedra are yellow, Zn(2) tetrahedra are green, H atoms are small blue circles, hydrogen bonds are thin black lines, (H₂O) groups are red circles.

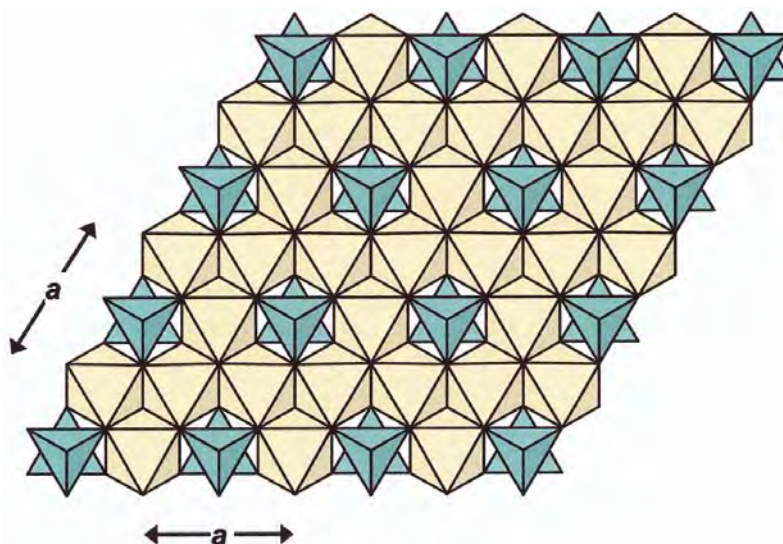


FIG. 2. The sheet of Zn(1) octahedra and Zn(2) tetrahedra in simonkolleite viewed down the *c* axis; legend as in Figure 1.

TABLE 5. MINERALS BASED ON DECORATED $[M^{2+}\phi_{2n}]$ SHEETS, ($M = \text{Cu}^{2+}, \text{Zn}$)

Mineral	Formula	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	Space gr.	Ref.
Simonkolleite	$[\text{Zn}_6 (\text{OH})_8 \text{Cl}_2] (\text{H}_2\text{O})$	6.3412(3)	<i>a</i>	23.646(1)	—	$R\bar{3}m$	(1)
Cianciulliite	$\text{Mn} (\text{Mg}, \text{Mn})_2 \text{Zn}_2 (\text{OH})_{10} (\text{H}_2\text{O})_{2-4}$	15.405(3)	6.344(1)	5.562(2)	101.23(2)	$C2/m$	(2)
Gordaite	$\text{Na} [\text{Zn}_4 (\text{SO}_4) (\text{OH})_6 \text{Cl}] (\text{H}_2\text{O})_6$	8.3556(3)	<i>a</i>	13.025(1)	—	$P\bar{3}$	(3)
Namuwite	$(\text{Zn}, \text{Cu}^{2+})_4 (\text{SO}_4) (\text{OH})_6 (\text{H}_2\text{O})_4$	8.331(6)	<i>a</i>	10.54(1)	—	$P\bar{3}$	(4)
Bechererite	$[\text{Zn}_7 \text{Cu}^{2+} \text{Si O}(\text{OH})_3 (\text{SO}_4) (\text{OH})_{13}]$	8.319(2)	<i>a</i>	7.377(1)	—	$P\bar{3}$	(5)
Chalcophyllite	$[\text{Cu}^{2+}_9 \text{Al} (\text{AsO}_4)_2 (\text{OH})_{12} (\text{H}_2\text{O})_6] (\text{SO}_4)_{1.5} (\text{H}_2\text{O})_{12}$	10.756	<i>a</i>	28.678	—	$R\bar{3}$	(6)
Ramsbeckite	$(\text{Cu}^{2+}, \text{Zn})_{15} (\text{OH})_{22} (\text{SO}_4)_4 (\text{H}_2\text{O})_6$	16.088(4)	15.576(4)	7.102(2)	90.22(2)	$P2_1/a$	(7)
Chalcophanite	$\text{Zn Mn}_3 \text{O}_7 (\text{H}_2\text{O})_3$	7.533(3)	<i>a</i>	20.794(7)	—	$R\bar{3}$	(8)
Claringbullite	$[\text{Cu}^{2+}_4 \text{Cl} (\text{OH})_6 (\text{Cl}_{0.29} (\text{OH})_{0.71})]$	6.6733(5)	<i>a</i>	9.185(1)	—	$P6_3/mmc$	(9)

References: (1) This work; (2) Grice & Dunn (1991); (3) Adiwidjaja *et al.* (1997); (4) Groat (1996); (5) Hoffmann *et al.* (1997); (6) Sabelli (1980); (7) Effenberger (1988); (8) Post & Appleman (1988); (9) Burns *et al.* (1995)

these structures is not immediately apparent from their formulae when expressed in the usual way (Table 5). However, we may rewrite these formulae by incorporating octahedrally coordinated vacancies and by identifying the decorating oxyanions and their mode of attachment to the sheet.

Cianciulliite

The formula of cianciulliite, $\text{Mn} (\text{Mg}, \text{Mn})_2 \text{Zn}_2 (\text{OH})_{10} (\text{H}_2\text{O})_{2-4}$, seems to be of the form $[M_5 \phi_{10}]$, but this is misleading as the Zn cations are tetrahedrally coordinated. Moreover, there is a vacancy in the sheet of octahedra, about which two tetrahedra are attached to the sheet at three ligands each (Fig. 4a) in the same

fashion as in simonkolleite. Rewriting the formula to reflect this feature gives $[^{16}(\text{Mn} \{\text{Mg}, \text{Mn}\}_2 \square) (\text{Zn} \{\text{OH}\}_4)_2 (\text{OH})_2] = [M_4 X_6 (\text{OH})_2]$ (where *X* represents simple anions of the decorating group) = $[M_4 \phi_8] = [M\phi_2]_4$.

Gordaite

The formula of gordaite, $\text{Na} [\text{Zn}_4 (\text{SO}_4) (\text{OH})_6 \text{Cl}] (\text{H}_2\text{O})_6$, is similarly deceptive, as the structural unit seems directly to be of the form $[M_4 \phi_8]$. However, gordaite has vacancies in the sheet of octahedra and one quarter of the Zn is tetrahedrally coordinated (Fig. 4b). If we rewrite the structural unit as $[\text{Zn}_8 (\text{SO}_4)_2 (\text{OH})_{12} \text{Cl}_2]$, six Zn cations are octahedrally coordinated, two

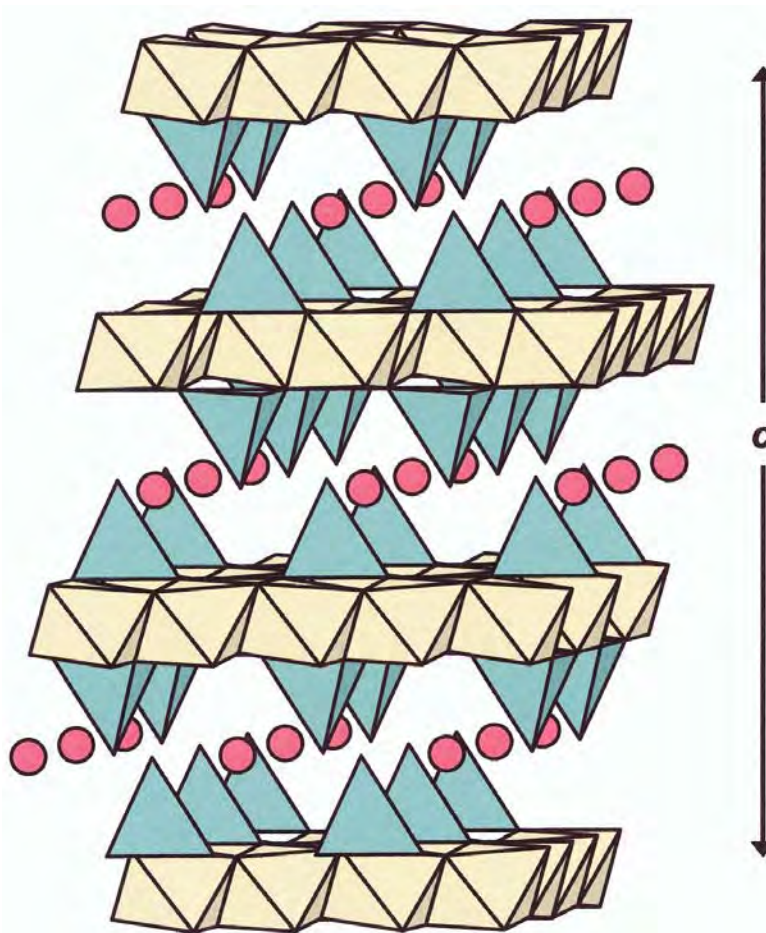


FIG. 3. Oblique view of the structure of simonkolleite, showing the conformation of adjacent sheets and the arrangement of the interstitial (H_2O) groups; legend as in Figure 1.

Zn cations are tetrahedrally coordinated, and there is one “octahedrally coordinated” vacancy in the sheet, which we can now write as $[\text{Zn}_6 \square] \{ \text{Zn}(\text{OH})_4 \}_2 (\text{SO}_4)_2 (\text{OH})_4 \text{Cl}_2$. The octahedrally coordinated species sum to seven; the (SO_4) groups link to two sheet anions, each $\{ \text{Zn}(\text{OH})_4 \}$ group links to three sheet anions, and with the additional four (OH) groups and two Cl anions, the total number of sheet anions sums to fourteen. Thus in gordaite, the sheet is $[M_7 X_8 \phi_6] = [M_7 \phi_{14}] = [M\phi_2]_7$; it is homeomorphic to graph 4b of Hawthorne & Schindler (2000).

Namuwite

The situation for namuwite is similar to that of gordaite. Six $(\text{Cu}^{2+}, \text{Zn})$ cations are octahedrally coordi-

nated, two Zn cations are tetrahedrally coordinated, and there is one octahedrally coordinated vacancy (cf. Fig. 4b). Thus $[(\text{Zn}, \text{Cu}^{2+})_4 (\text{SO}_4) (\text{OH})_6] \times 2 \rightarrow [(\text{Zn}, \text{Cu}^{2+})_8 (\text{SO}_4)_2 (\text{OH})_{12}] \rightarrow [\text{Zn}_6 \square] \{ \text{Zn}(\text{OH})_4 \}_2 (\text{SO}_4)_2 (\text{OH})_6$. The octahedrally coordinated cations sum to seven; the (SO_4) groups link to two sheet anions, each $\{ \text{Zn}(\text{OH})_4 \}$ tetrahedron bonds to three sheet anions, and there are an additional six (OH) groups, resulting in fourteen sheet anions. Thus in namuwite, the sheet is $[M_7 X_8 \phi_6] = [M_7 \phi_{14}] = [M\phi_2]_7$; it is homeomorphic to graph 4b of Hawthorne & Schindler (2000).

Bechererite

In bechererite, there are six octahedrally coordinated $(\text{Zn}, \text{Cu}^{2+})$ cations, every seventh octahedron is vacant,

and there are two tetrahedrally coordinated Zn cations (Fig. 4c), and we may write the sheet formula as $[(^{16})\{\text{Zn,Cu}^{2+}\} \phi] \{\text{Zn}_2 (\text{OH})_7\} (\text{SO}_4) (\text{Si O} \{\text{OH}\}_3) (\text{OH})_6]$. The tetrahedrally coordinated Zn forms a $[T_2 \text{O}_7]$ pyro-group in which all non-bridging bonds involve anions of the sheet (*i.e.*, the pyro-group links adjacent

sheets). Thus there are six sheet anions involved in the pyro-group, one anion for each of the (SO_4) and $(\text{Si}_2 \{\text{OH}\}_3)$ groups, and six (OH) groups, a total of fourteen anions. Thus in bechererite, the sheet is $[M_7 X_8 \phi_6] = [M_7 \phi_{14}] = [M\phi_2]_7$; it is homeomorphic to graph 4b of Hawthorne & Schindler (2000).

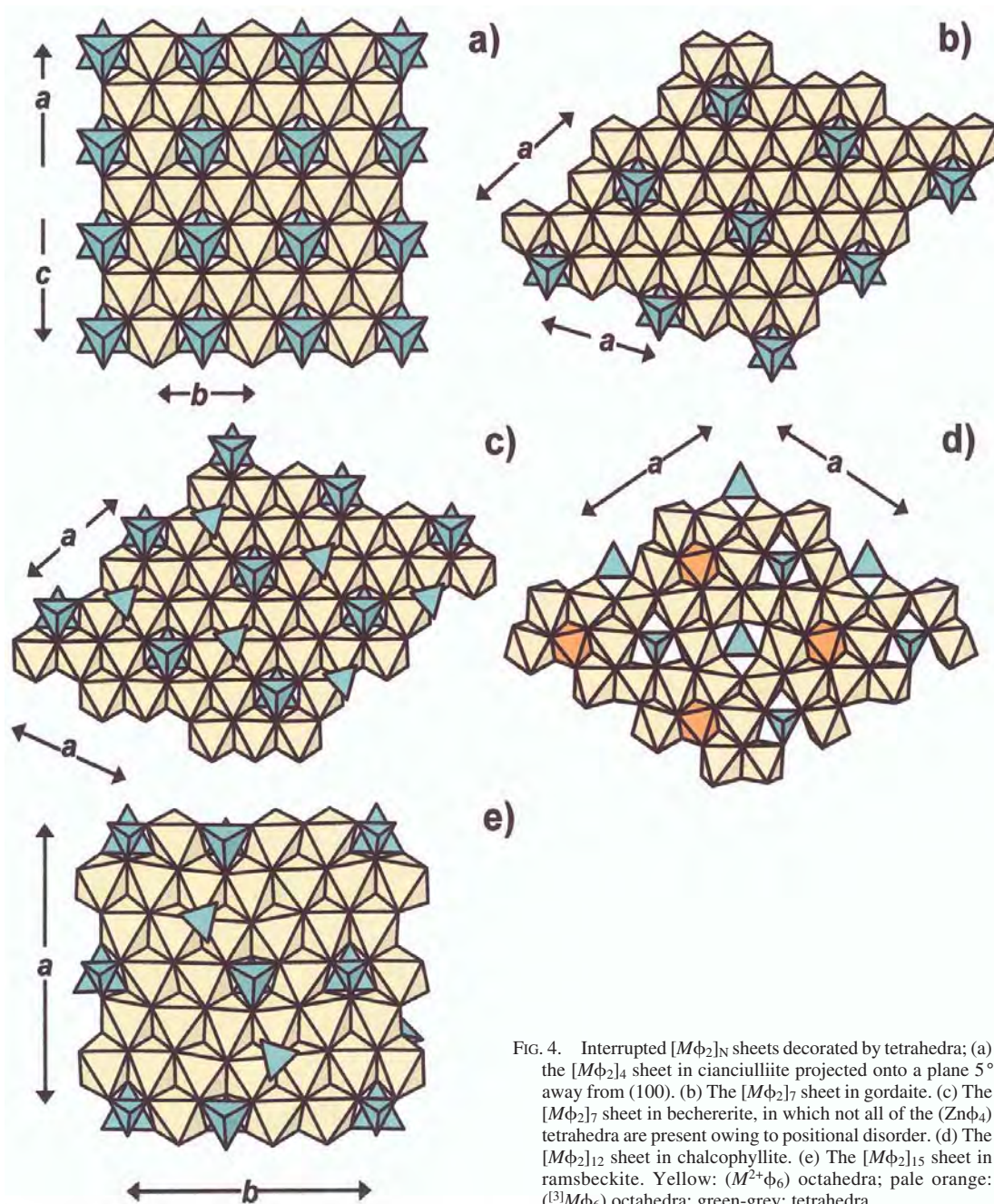


FIG. 4. Interrupted $[M\phi_2]_N$ sheets decorated by tetrahedra; (a) the $[M\phi_2]_4$ sheet in ciangiulite projected onto a plane 5° away from (100). (b) The $[M\phi_2]_7$ sheet in gordaite. (c) The $[M\phi_2]_7$ sheet in bechererite, in which not all of the $(\text{Zn}\phi_4)$ tetrahedra are present owing to positional disorder. (d) The $[M\phi_2]_{12}$ sheet in chalcophyllite. (e) The $[M\phi_2]_{15}$ sheet in ramsbeckite. Yellow: $(M^{2+}\phi_6)$ octahedra; pale orange: $(^{13})M\phi_6$ octahedra; green-grey: tetrahedra.

Chalcophyllite

The formula of chalcophyllite may be written as $[\text{Cu}^{2+}_9 \text{Al} (\text{AsO}_4)_2 (\text{OH})_{12} (\text{H}_2\text{O})_6] (\text{SO}_4)_{1.5} (\text{H}_2\text{O})_{12}$, where the decorated sheet is within the square brackets and the species outside the square brackets are interstitial. Each (AsO_4) group is attached to the sheet by three vertices and is associated with a vacancy in the octahedra of the sheet (Fig. 4d). Thus the octahedrally coordinated species are $(\text{Cu}^{2+}_9 \square_2 \text{Al})$, and we may write the sheet formula as $[(\text{Cu}^{2+}_9 \square_2 \text{Al}) (\text{AsO}_4)_2 (\text{OH})_{12} (\text{H}_2\text{O})_6] = [M_{12} X_6 \phi_{18}] = [M_{12} \phi_{24}] = [M\phi_2]_{12}$; it is homeomorphic to graph 4c of Hawthorne & Schindler (2000).

Ramsbeckite

We write the formula as $(\text{Cu}^{2+}_{13}\text{Zn}_2) (\text{OH})_{22} (\text{SO}_4)_4 (\text{H}_2\text{O})_6$. There are two Zn cations *pfu* (per formula unit) in tetrahedral coordination. Furthermore, the $(\text{Zn}\phi_4)$ tetrahedron shares three anions with the sheet and the fourth anion with an (SO_4) group of an adjacent sheet: $\{\text{Zn S}\phi_7\}$, and another (SO_4) group shares one anion with the sheet (Fig. 5b). We may thus write the formula as $[(\text{Cu}^{2+}_{13}\text{Zn}_2) \square_2] \{\text{Zn} (\text{OH})_3 \text{SO}_4\}_2 (\text{SO}_4)_2 (\text{OH})_{16} (\text{H}_2\text{O})_6 = [M_{15} X_4 \phi_{16}] = [M_{15} \phi_{30}] = [M\phi_2]_{15}$; it is homeomorphic to graph 4d of Hawthorne & Schindler (2000).

Chalcophanite

The formula of chalcophanite, $\text{Zn Mn}_3 \text{O}_7 (\text{H}_2\text{O})_3$, does not seem to be related to the $[M\phi_2]_N$ structures.

However, although all of the cations are octahedrally coordinated, only the Mn^{4+} cations form a sheet of octahedra. Moreover, there is one vacancy for each six Mn^{4+} cations in the structure, indicating that chalcophanite has an interrupted sheet (Fig. 5a). Thus we may rewrite the formula in the following way: $[\text{Zn Mn}_3 \text{O}_7 (\text{H}_2\text{O})_3] \times 2 \rightarrow [\text{Mn}_6 \text{Zn}_2 \text{O}_{14} (\text{H}_2\text{O})_6] = [^{[6]}(\text{Mn}_6 \square) ^{[6]}(\text{Zn O}_3 \{\text{H}_2\text{O}\}_3)_2 \text{O}_8]$. The octahedrally coordinated species within the sheet sum to seven; each $(\text{Zn O}_3 \{\text{H}_2\text{O}\}_3)$ octahedron shares three anions with the sheet, overlying the vacant octahedra of the sheet, and the total number of sheet anions is fourteen: $[M_7 X_6 \phi_8] = [M_7 \phi_{14}] = [M\phi_2]_7$.

Claringbullite

The formula for claringbullite is rather deceptive. If written as in Table 5, $[\text{Cu}^{2+}_4 \text{Cl} (\text{OH})_6 \{\text{Cl}, \text{OH}\}]$, it seems to be of the form $[^{[6]}(\text{Cu}^{2+}_4 \phi_8) = [M\phi_2]_4$. However, in the sheet of octahedra in claringbullite, there is an octahedrally coordinated vacancy, $\square$, and only three of the four Cu^{2+} cations in the unit formula are octahedrally coordinated. The other Cu^{2+} cation is not part of the sheet; it has trigonal prismatic coordination and links adjacent sheets (Fig. 5b), *i.e.*, it decorates the sheet of octahedra. Thus we may write the formula of claringbullite more comprehensively as $[(\text{Cu}^{2+}_3 \square) <\text{Cu} (\text{OH})_6> \text{Cl} (\text{Cl}, \text{OH})] = [M_4 X_6 \phi_2] = [M_4 \phi_8] = [M\phi_2]_4$; it is homeomorphic to graph 3c of Hawthorne & Schindler (2000).

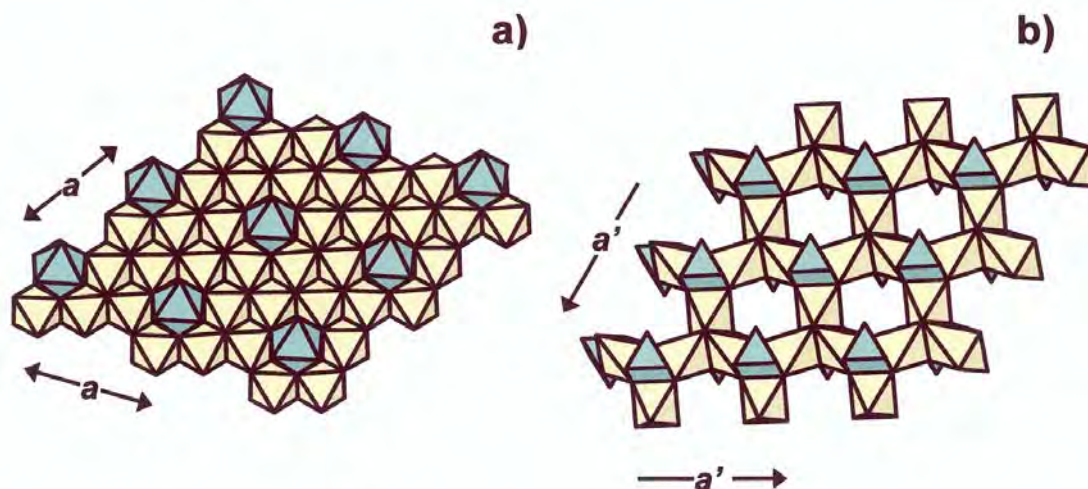


FIG. 5. Interrupted $[M\phi_2]_N$ sheets decorated by other polyhedra: (a) the $[M\phi_2]_7$ sheet in chalcophanite, decorated by $(\text{Zn}\phi_6)$ octahedra. (b) The $[M\phi_2]_4$ sheet in claringbullite, decorated by $(\text{Cu}^{2+}\phi_6)$ triangular prisms; the direction of projection for claringbullite is tilted slightly from the *c* axis also that the triangular-prismatic coordination of the decorating species is apparent. Yellow: octahedra of the sheet; green-grey: decorating species.

SUMMARY

Simonkolleite, $[\text{Zn}_3\text{Cl}] \{[\text{Zn}(\text{OH})_3\text{Cl}]_2(\text{OH})_2\} (\text{H}_2\text{O})$, is a decorated $[\text{M}\phi_2]_N$ sheet structure with an interrupted sheet, $N = 4$, and Zn in both octahedral and tetrahedral coordination. Also in this family of structures are ciangiullite, gordaite, namuwite, bechererite, chalcophyllite, ramsbeckite, chalcophanite and claringbullite.

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REFERENCES

- ADIWIDJAJA, G., FRIESE, K. KLASKA, K.-H. & SCHLÜTER, J. (1997): The crystal structure of gordaite $\text{NaZn}_4(\text{SO}_4)(\text{OH})_6\text{Cl}\cdot 6\text{H}_2\text{O}$. *Z. Kristallogr.* **212**, 704-707.
- ALLMANN, R. (1968): Verfeinerung der Struktur des Zinkhydroxidchlorids. II. $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot 1\text{H}_2\text{O}$. *Z. Kristallogr.* **126**, 417-426.
- BROWN, I.D. & ALTERMATT, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41**, 244-247.
- BURNS, P.C., COOPER, M.A. & HAWTHORNE, F.C. (1995): Claringbullite: a Cu^{2+} oxysalt with Cu^{2+} in trigonal-prismatic coordination. *Can. Mineral.* **33**, 633-639.
- _____ & HAWTHORNE, F.C. (1995): Coordination-geometry structural pathways in Cu^{2+} oxysalt minerals. *Can. Mineral.* **33**, 889-905.
- COOPER, M.A. & HAWTHORNE, F.C. (2001): Structure topology and hydrogen bonding in marthozite, $\text{Cu}^{2+}[(\text{UO}_2)_3(\text{SeO}_3)_2\text{O}_2](\text{H}_2\text{O})_6$, a comparison with guilleminite, $\text{Ba}[(\text{UO}_2)_3(\text{SeO}_3)_2\text{O}_2](\text{H}_2\text{O})_3$. *Can. Mineral.* **39**, 797-807.
- EBY, R.K. & HAWTHORNE, F.C. (1989a): Cornetite, a modulated densely-packed Cu^{2+} oxysalt. *Mineral. Petrol.* **40**, 127-136.
- _____ & _____ (1989b): Euchroite, a heteropolyhedral framework structure. *Acta Crystallogr.* **C45**, 1479-1482.
- _____ & _____ (1990): Clinoclase and the geometry of [5]-coordinate Cu^{2+} in minerals. *Acta Crystallogr.* **C46**, 2291-2294.
- _____ & _____ (1993): Structural relations in copper oxysalt minerals. I. Structural hierarchy. *Acta Crystallogr.* **B49**, 28-56.
- EFFENBERGER, H. (1988): Ramsbeckite, $(\text{Cu,Zn})_{15}(\text{OH})_{22}(\text{SO}_4)_4\cdot 6\text{H}_2\text{O}$: revision of the chemical formula based on a structure determination. *Neues Jahrb. Mineral., Monatsh.*, 38-48.
- GRICE, J.D. & DUNN, P.J. (1991): The crystal structure of ciangiullite, $\text{Mn}(\text{Mg,Mn})_2\text{Zn}_2(\text{OH})_{10}\cdot 2-4\text{H}_2\text{O}$. *Am. Mineral.* **76**, 1711-1714.
- GROAT, L.A. (1996): The crystal structure of namuwite, a mineral with Zn in tetrahedral and octahedral coordination, and its relationship to the synthetic basic zinc sulfates. *Am. Mineral.* **81**, 238-243.
- HAWTHORNE, F.C. (1985): Refinement of the crystal structure of botallackite. *Mineral. Mag.* **49**, 87-89.
- _____ & GROAT, L.A. (1985): The crystal structure of wroewolfeite, a mineral with $[\text{Cu}_4(\text{OH})_6(\text{SO}_4)(\text{H}_2\text{O})]$ sheets. *Am. Mineral.* **70**, 1050-1055.
- _____ & SCHINDLER, M. (2000): Topological enumeration of decorated $[\text{Cu}^{2+}\phi_2]_N$ sheets in hydroxy-hydrated copper-oxysalt minerals. *Can. Mineral.* **38**, 751-761.
- HOFFMANN, C., ARMBRUSTER, T. & GIESTER, G. (1997): Acentric structure (P3) of bechererite, $\text{Zn}_7\text{Cu}(\text{OH})_{13}[\text{SiO}(\text{OH})_3\text{SO}_4]$. *Am. Mineral.* **82**, 1014-1018.
- INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY, VOL. C (1992): Kluwer Academic Publishers, Dordrecht, The Netherlands.
- NOWACKI, W. & SILVERMAN, J.N. (1961): Die Kristallstruktur von Zinkhydroxychlorid. II. $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot 1\text{H}_2\text{O}$. *Z. Kristallogr.* **115**, 21-51.
- POST, J.E. & APPLEMAN, D.E. (1988): Chalcophanite, $\text{ZnMn}_3\text{O}_7\cdot 3\text{H}_2\text{O}$: new crystal-structure determinations. *Am. Mineral.* **73**, 1401-1404.
- SABELLI, C. (1980): The crystal structure of chalcophyllite. *Z. Kristallogr.* **151**, 129-140.
- SCHMETZER, K., SCHNORRER-KÖHLER, G. & MEDENBACH, O. (1985): Wülfingite, $\epsilon\text{-Zn}(\text{OH})_2$, and simonkolleite, $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot \text{H}_2\text{O}$, two new minerals from Richelsdorf, Hesse, F.R.G. *Neues Jahrb. Mineral., Monatsh.*, 145-154.

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THE STRUCTURE OF SIMONKOLLEITE

APPENDIX 1

TABLE 4. BOND-VALENCE (ν) TABLE FOR SIMONKOLLEITE

	Zn(1)	Zn(2)	Σ	H(1)	H(2)	H[3]	Σ
O(1)	0.29 ^{x4} ↓ ^{x2} →	0.51 ^{x3} →	1.09	0.9			1.99
O(2)	0.37 ^{x2} ↓ ^{x3} →		1.11		0.9		2.01
O(3)			—		0.1 ^{x2} →	0.9 ^{x2} →	2.00
Cl		0.44	0.44	0.1 ^{x3} →		0.1	0.84
Σ	1.90	1.97		1.0	1.0	1.0	

Calculated with the curves of Brown & Altermatt (1985)