

## The crystal structure of philolithite, a trellis-like open framework based on cubic closest-packing of anions

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### ABSTRACT

The crystal structure of philolithite,  $\text{Pb}_{12}\text{O}_6\text{Mn}(\text{Mg},\text{Mn})_2(\text{Mn},\text{Mg})_4(\text{SO}_4)(\text{CO}_3)_4\text{Cl}_4(\text{OH})_{12}$ ,  $P4_2/nmm$ ,  $a = 12.627(9)$ ,  $c = 12.595(9)$  Å,  $V = 2008(2)$  Å<sup>3</sup>,  $Z = 2$  has been solved by Patterson difference-Fourier syntheses and refined to  $R = 0.053$  for 814  $F_o > 4\sigma_{F_o}$  using  $\text{MoK}\alpha$  X-ray data. In the structure,  $\text{MnO}_6$  octahedra form straight chains parallel to  $[110]$  and  $[\bar{1}\bar{1}0]$  by sharing opposite octahedral edges. Octahedra within the chains are further linked by sharing free corners with  $\text{MnO}_4$  and  $\text{SO}_4$  tetrahedra and  $\text{CO}_3$  triangles. The  $\text{MnO}_4$  and  $\text{SO}_4$  tetrahedra also form bridging struts between octahedral chains, connecting them in the  $[001]$  direction into an open framework. The Pb, Cl, and non-framework O atoms occupy the open spaces within the framework. The 10- and 12-fold coordinations of the Pb atoms exhibit the lone-pair effect. Pb atoms link via short bonds to non-framework O atoms to form chains parallel to  $[110]$  and  $[\bar{1}\bar{1}0]$ . When viewed down  $[111]$ ,  $[\bar{1}\bar{1}1]$ ,  $[1\bar{1}\bar{1}]$ , or  $[\bar{1}\bar{1}\bar{1}]$ , the framework (less the  $\text{CO}_3$  groups) is seen to be based upon cubic closest-packing of anions. This open framework of composition  $[\text{Mn},\text{Mg}]_{12}^{2+}[\text{SO}_4]_2^{2-}[\text{Mn}^{2+}\text{O}_4]_2^{2-}\text{O}_8(\text{OH})_{24}^{32-}$ , referred to as a closest-packed trellis, is the fundamental unit for the structure.

### INTRODUCTION

The new mineral philolithite from the Långban mines, Filipstad district, Värmland, Sweden (see Holtstam and Langhof 1999), was described by Kampf et al. (1998). The initial powder and single-crystal X-ray diffraction and EDS chemical analysis of philolithite, which confirmed it to be a new species, were conducted on crystals on a specimen obtained from the Swedish Museum of Natural History in 1965–66 by one of the authors (P.B.M.). This specimen, now designated as one of the cotypes, is in the collection of the Los Angeles County Museum of Natural History (LACMNH no. 41794). The crystal upon which an initial structure determination was attempted came from a second co-type specimen, provided by William W. Pinch, and now in the collection of the Canadian Museum of Nature (CMN no. 58623). The low quality of this crystal coupled with absorption effects only allowed an approximate solution of the structure. Subsequently, the new species was identified on other specimens in the collection of the Swedish Museum of Natural History. A crystal from one of these specimens (SMNH no. 37389), also designated as a cotype, allowed the complete solution and refinement of the crystal structure reported herein.

### STRUCTURE DETERMINATION

Single-crystal X-ray precession and four-circle diffractometer studies showed philolithite to be tetragonal, space group  $P4_2/nmm$ ,  $a = 12.627(9)$ ,  $c = 12.595(9)$  Å,  $V = 2008(2)$  Å<sup>3</sup>,  $Z = 2$ . The cell parameters were obtained by least-squares refinement

from the setting angles of 25 reflections between  $2\theta = 18^\circ$  and  $28^\circ$ , automatically centered by the diffractometer.

X-ray intensity data were collected on a Huber four-circle diffractometer using a crystal of philolithite ground to a spheroid of dimensions  $75 \times 70 \times 55 \mu\text{m}^3$ . The operating conditions were: room temperature, 45 kV, 25 mA, graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069$  Å), scan mode  $\omega - 2\theta$ , scan width  $3^\circ(2\theta)$ , scan speed  $3^\circ/\text{min}$ ,  $2\theta_{\text{max}} = 60^\circ$ , three standard reflections measured every one hundred reflections. The 6139 measured intensities ( $0 \leq h \leq 17$ ,  $-17 \leq k \leq 17$ ,  $0 \leq l \leq 17$ ) were corrected for Lorentz and polarization effects and an absorption correction by the  $\psi$ -scan method was applied. The final data set reduced to 1568 unique reflections.

The metal atoms (Pb, Mn, Mg) were readily located by Patterson synthesis and the positions of the other atoms were obtained from subsequent difference-Fourier syntheses. Lead was assigned to two sites, Pb1 and Pb2. The other three metal sites, M1, M2, and M3 were assumed to contain only Mn for the initial refinements. In later refinements the allotments of Mn and Mg to the M1, M2, and M3 sites were refined. Based upon the results, the M1 (fourfold-coordinated) site was assigned full occupancy by Mn alone, the M2 site assigned full occupancy by 54% Mg and 46% Mn, and the M3 site was assigned full occupancy by 68% Mn and 32% Mg. Over the three sites this yields  $(\text{Mn}_{4.64}, \text{Mg}_{2.36})_{27}$ . Electron microprobe analyses reported in Kampf et al. (1998) for crystals from the same specimen (SMNH no. 37389) provide  $(\text{Mn}_{4.24}, \text{Mg}_{2.42})_{26.66}$ .

The structure was refined in space group  $P4_2/nmm$  (second setting with origin on  $2/m$ ) with the SHELXL-93 program (Sheldrick 1993). In the final cycles anisotropic displacement parameters for Pb, Mn, Mg, S, and Cl and isotropic displacement parameters for C and O atoms were refined. The final

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**TABLE 1.** Positional and displacement parameters for philolithite

Atom	x	y	z	U*
Pb1	0.05999(6)	-0.05999(6)	0.61863(9)	0.0141(3)
Pb2	0.40559(6)	0.26285(6)	0.59807(6)	0.0130(2)
M1	3/4	1/4	3/4	0.016(2)
M2	0	0	0	0.015(3)
M3	0.1660(3)	-0.1660(3)	0.9841(5)	0.012(2)
S	3/4	1/4	1/4	0.014(3)
C	0.092(2)	-0.092(2)	0.211(2)	0.011(6)
O1	0.682(1)	-0.682(1)	0.184(2)	0.024(6)
O2	0.152(1)	-0.152(1)	0.160(2)	0.027(6)
O3	0.027(3)	-0.027(3)	0.160(2)	0.022(5)
O4	0.092(2)	-0.092(2)	0.313(2)	0.032(6)
O5	1/4	1/4	0	0.014(6)
O6	0.083(1)	0.083(1)	0.50000	0.005(3)
OH7	0.167(1)	-0.167(1)	0.497(2)	0.014(4)
OH8	0.166(1)	0.003(1)	0.970(1)	0.012(3)
Cl	0.0968(7)	1/4	1/4	0.023(2)

Note: The M2 site composition refined to 46(5)% Mn and 54(5)% Mg. The M3 site composition refined to 68(3)% Mn and 32(4)% Mg. \*  $U_{iso}$  (for C and O atoms) is defined as  $\exp(-8\pi^2 U[\sin(\theta)/\lambda]^2)$ .  $U_{eq}$  (for Pb, M, S, and Cl atoms) is defined as  $(U_{11} + U_{22} + U_{33})/3$ .

refinement yielded a conventional  $R$  index of 0.053 for 814 measured reflections with  $F_o > 4\sigma_{F_o}$  (0.144 for all 1568 data),  $wR2 = 0.134$  [weighted  $R$  factor on  $F^2$ , as defined by Sheldrick (1993)], goodness of fit = 0.935. Maximum and minimum heights in the final difference-Fourier synthesis are +2.58 and -2.95  $e/\text{\AA}^3$ . No peaks were found that could be reasonably assigned to H atoms based on geometrical considerations.

Table 1 includes the final fractional coordinates and equivalent isotropic displacement parameters, Table 2 the anisotropic displacement parameters, Table 3<sup>1</sup> the observed and calculated structure factors, Table 4 interatomic distances and angles, and Table 5 the bond valences.

**TABLE 2.** Anisotropic displacement parameters for philolithite

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Pb1	0.0142(3)	0.0142(3)	0.0139(5)	0.0003(3)	-0.0003(3)	0.0015(5)
Pb2	0.0141(4)	0.0140(4)	0.0110(3)	0.0013(3)	-0.0013(3)	0.0004(3)
M1	0.018(3)	0.018(3)	0.012(4)	0	0	0
M2	0.014(4)	0.014(4)	0.019(6)	-0.003(3)	0.003(3)	-0.008(4)
M3	0.011(2)	0.011(2)	0.012(3)	0.001(2)	-0.001(2)	-0.000(2)
S	0.016(5)	0.016(5)	0.012(6)	0	0	0
Cl	0.025(5)	0.032(5)	0.012(2)	-0.004(3)	0	0

Note: Anisotropic displacement parameters are of the form:  $\exp(-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}))$ .

**TABLE 4.** Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in philolithite

Pb1-O6 $\times 2$	2.364(11)	M1-O2 $\times 4$	2.09(3)	M3-O1	2.14(3)	S-O1 $\times 4$	1.48(2)
Pb1-OH7	2.454(24)	O2-M1-O2 $\times 4$	107.4(7)	M3-OH8 $\times 2$	2.14(2)	O1-S-O1 $\times 4$	108(1)
Pb1-O4	2.846(26)	O2-M1-O2 $\times 2$	113.8(14)	M3-O2	2.22(3)	O1-S-O1 $\times 2$	112(2)
Pb1-O3	3.189(24)			mean	2.15		
Pb1-O1	3.301(26)			OH7-M3-OH7	88.4(10)		
Pb1-Cl $\times 2$	3.523(3)	M2-O3 $\times 2$	2.07(2)	OH8-M3-OH8	89.6(8)	C-O2	1.24(4)
Pb1-O1 $\times 2$	3.699(26)	M2-OH8 $\times 4$	2.13(1)	O2-M3-OH7 $\times 2$	88.2(8)	C-O4	1.29(4)
Pb1-OH8 $\times 2$	3.724(14)	mean	2.11	O1-M3-OH8 $\times 2$	90.7(6)	C-O3	1.33(4)
		O3-M2-OH8 $\times 4$	89.3(6)	OH7-M3-OH8 $\times 2$	91.0(5)	mean	1.29
		O3-M2-OH8 $\times 4$	90.7(6)	O1-M3-OH7 $\times 2$	91.1(8)	O2-C-O4	122(3)
Pb2-O6	2.308(12)	OH8-M2-OH8 $\times 2$	89.8(8)	O2-M3-OH8 $\times 2$	90.0(6)	O2-C-O3	120(3)
Pb2-O5	2.326(1)	OH8-M2-OH8 $\times 2$	90.2(8)			O3-C-O4	118(3)
Pb2-OH8	2.329(14)	M3-OH7 $\times 2$	2.12(2)				
Pb2-O4	3.187(14)						
Pb2-Cl	3.265(6)					OH7-H...O4	2.68(4)
Pb2-O3	3.440(17)					OH8-H...Cl	3.20(2)
Pb2-Cl	3.452(6)						
Pb2-O2	3.496(18)						
Pb2-OH8	3.511(14)						
Pb2-OH7	3.623(9)						

Notes: M1 =  $\text{Mn}^{2+}$ ; M2 = 46%  $\text{Mn}^{2+}$  + 54%  $\text{Mg}^{2+}$ ; M3 = 68%  $\text{Mn}^{2+}$  + 32%  $\text{Mg}^{2+}$ .

## DESCRIPTION OF THE CRYSTAL STRUCTURE

In terms of polyhedral linkages, the dominant structural elements in philolithite are straight chains consisting of  $\text{MnO}_6$  octahedra sharing opposite octahedral edges. Adjacent octahedra within the chains are further linked by sharing free corners with  $\text{MnO}_4$  and  $\text{SO}_4$  tetrahedra and  $\text{CO}_3$  triangles. To accommodate these peripheral links with polyhedral size differences, the octahedra in the chains are canted to and fro (Fig. 1). The chains are skewed at  $90^\circ$ , running parallel to  $[110]$  and  $[\bar{1}10]$ . The  $\text{MnO}_4$  and  $\text{SO}_4$  tetrahedra form bridging struts between the octahedral chains, connecting them in the  $[001]$  direction into an open three-dimensional framework. Atoms of Pb, Cl, and O occupy spaces within the framework. The structure is viewed down  $[\bar{1}10]$  in Figure 2 and down  $[001]$  in Figure 3.

### Carbonate and sulfate groups

The triangular carbonate group is rather regular in shape, with C in the plane of the triangle and O-O distances of 2.21(4), 2.23(4), and 2.25(4)  $\text{\AA}$ ; however, C is displaced from the center of the triangle, away from O3 and toward O2 (C-O2 = 1.24, C-O3 = 1.33, C-O4 = 1.29  $\text{\AA}$ ). There is no obvious explanation for the shift of the C; it is actually shifted toward the nearest cation M1 with C-M1 = 2.85  $\text{\AA}$  and O2 is valence oversatu-

<sup>1</sup>For a copy of Table 3, document item AM-99-045, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site (<http://www.minsocam.org> or current web address).

TABLE 5. Bond valences for philolithite

	O1	O2	O3	O4	O5	O6	OH7	OH8	Cl	$\Sigma_v$
Pb1	0.04 $\times 2$ 0.01 $\times 2$		0.05	0.14		0.51 $\times 2$	0.40	$\times 2$ 0.01	$\times 2$ 0.07 $\times 2$	1.83
Pb2		0.02 $\times 2$	0.03 $\times 2$	0.06 $\times 2$	0.56 $\times 4$	0.59 $\times 2$	0.02 $\times 2$	0.56 0.02	0.08 $\times 2$ 0.14 $\times 2$	2.08
M1		$\times 4$ 0.44 $\times 4$								1.76
M2			$\times 2$ 0.40					$\times 4$ 0.35		2.20
M3	0.36	0.29					$\times 2$ 0.38 $\times 2$	$\times 2$ 0.36		2.13
S	$\times 4$ 1.49									5.96
C		1.49	1.17	1.32						3.98
H1				0.21			0.79			1.00
H2								0.82	0.18 $\times 2$	1.00
$\Sigma_v$	1.91	2.26	1.68	1.79	2.24	2.20	1.99	2.12	0.94	

Notes: The multiplicities are the number of equivalent bonds for each cation (left) and for each anion (right). Constants from Brese and O'Keeffe (1991). Constants for M2 and M3 sites are based upon Mn and Mg compositions obtained from the structure refinement. Hydrogen bond valence based upon Brown and Altermatt (1985). Note that the OH8-Cl bond distance of 3.2 Å was taken as equivalent to a O-O bond distance of 2.8 Å for purposes of assigning OH8-H...Cl bond valences.

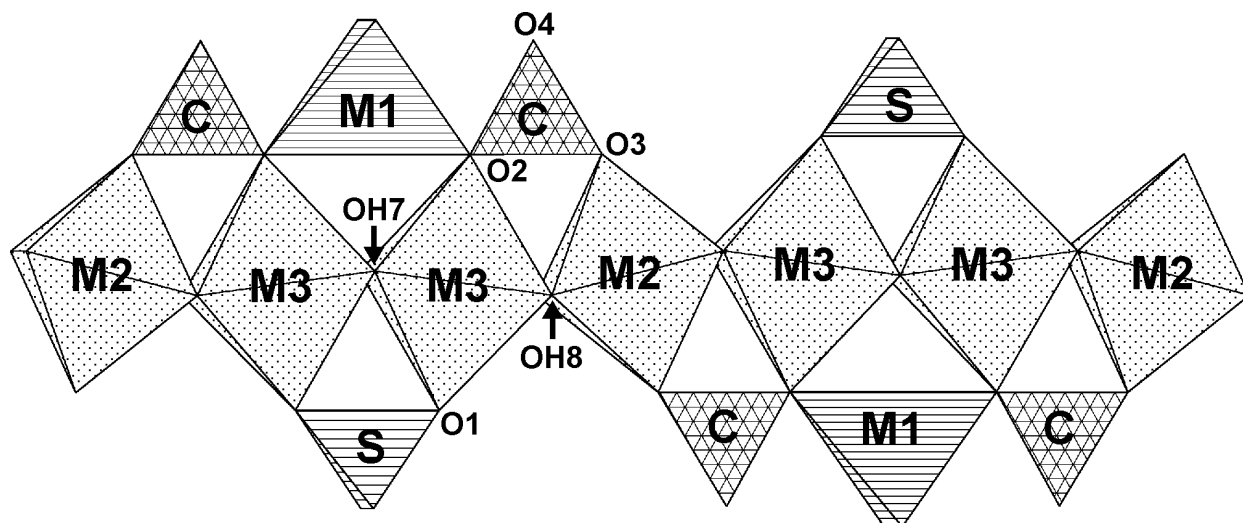


FIGURE 1. Octahedral chain and peripheral polyhedra in philolithite. The orientation is slightly canted to that in Figure 2.

rated, while O3 and O4 are undersaturated. The sulfate group is quite regular with four equivalent S-O1 bonds and O1-S-O1 angles between 108° and 112°.

### M1 tetrahedron

As noted above, the structure refinement showed the M1 site to be occupied completely by Mn. Bond valences show the Mn to be in the divalent state. The site is surrounded by four O atoms forming a slightly distorted tetrahedron. This is one of very few reported occurrences of tetrahedral coordination of O about Mn<sup>2+</sup> in a mineral structure (e.g., katoptrite; Moore et al. 1976). The four Mn-O2 bonds of 2.09 Å are significantly shorter than those generally reported for Mn<sup>2+</sup>-O in octahedral coordinations, but are comparable to those reported for Mn<sup>2+</sup>-O in tetrahedral coordinations in other compounds (e.g., <sup>14</sup>Mn4-O 2.08 and <sup>14</sup>Mn5-O 2.04 Å in katoptrite).

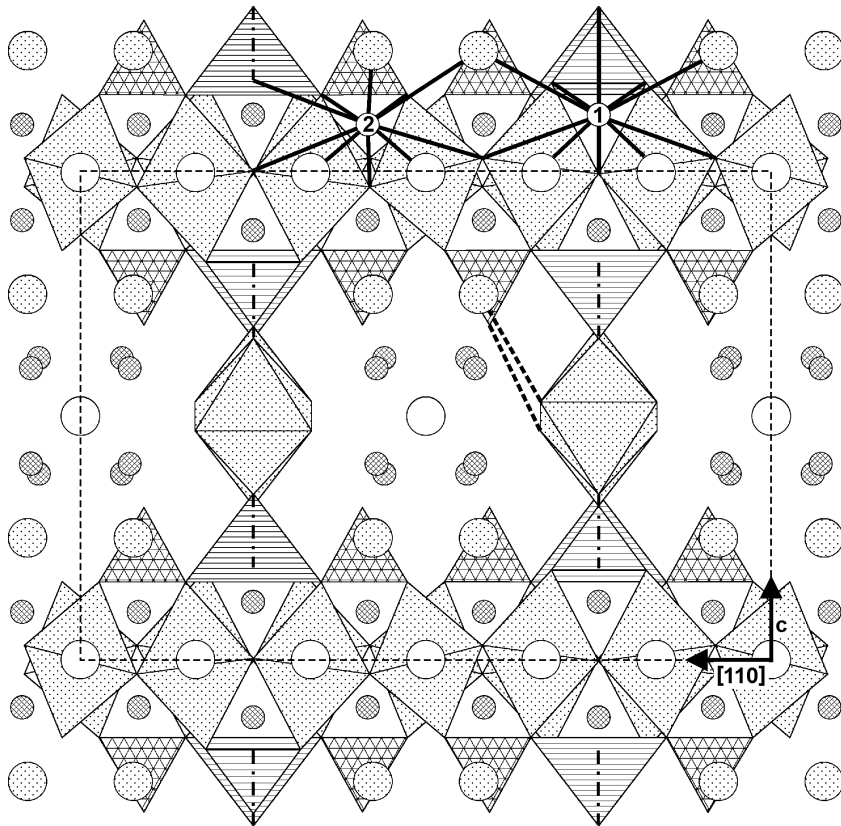
### M2 and M3 octahedra

The M2 site, assigned full occupancy by 54% Mg and 46% Mn, and the M3 site, assigned full occupancy by 68% Mn and

32% Mg, are both octahedrally coordinated. The average M-O distances, 2.11 and 2.15 Å respectively, are consistent with the refined compositions of these sites. The M2 octahedron is notably squat in aspect with short apical M2-O3 bonds of 2.07 Å. This is consistent with O3 being the most bond-undersaturated anion [1.68 valence units (v.u.)] in the structure. In the M3 octahedron, the M3-O2 bond of 2.22 Å is much longer than the rest and this is consistent with O2 being the most bond oversaturated anion (2.26 v.u.).

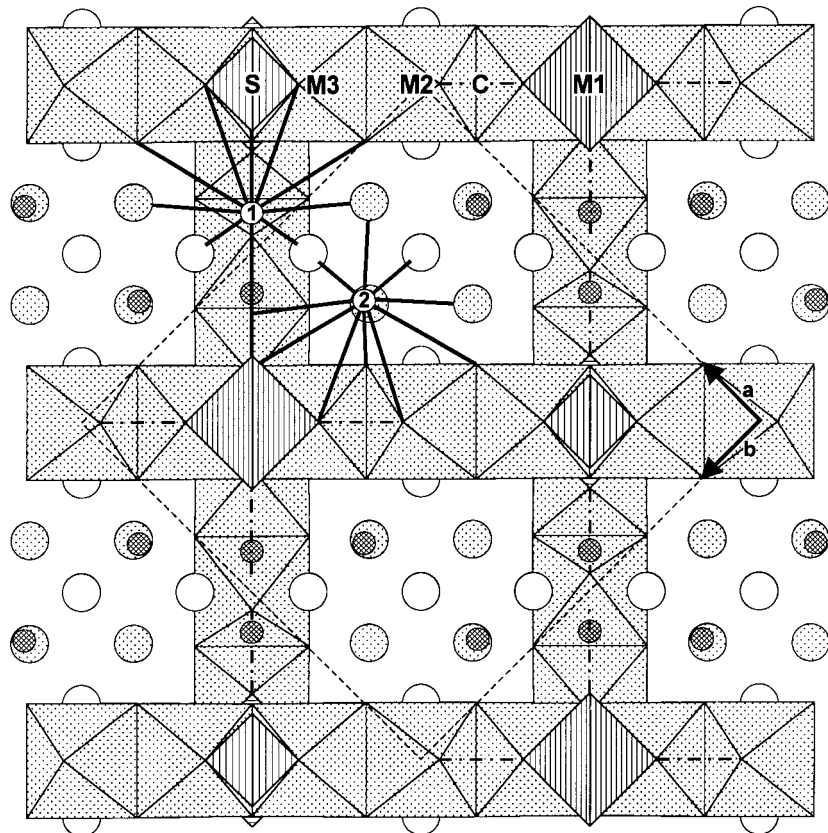
### Pb coordinations

In highly distorted Pb<sup>2+</sup>O<sub>n</sub> (O = anion) polyhedra, choice of coordination number can be somewhat arbitrary and we have selected the following upper limits. Pb1 bonds to ten O and two Cl atoms. Pb2 bonds to eight O and two Cl atoms. The Pb-O bond lengths vary greatly, from 2.36 to 3.72 Å for Pb1 and from 2.31 to 3.62 Å for Pb2. Pb-Cl bond distances fall within a much narrower range, 3.27 to 3.52 Å for both coordinations. Each Pb coordination is characterized by three short Pb-O bonds and these are arranged on the same side of their respective Pb



**FIGURE 2.** Atomic structure of philolithite viewed along  $[\bar{1}10]$ . Small cross-hatched circles = Pb (two Pb are uncross-hatched and labeled 1 and 2); large stippled circles = Cl; large open circles = O. See Figure 1 for identification of polyhedra.  $\text{CO}_3$  groups on edge are shown with dot-dash lines.

**FIGURE 3.** Atomic structure of philolithite viewed along  $[001]$ . The unit cell is outlined by a dashed line.



atoms. This is a clear demonstration of the lone-pair effect (Moore et al. 1993) in which the Pb electron lone-pair ( $\Psi^2$ ) is presumed to be localized on the side of the Pb atom opposite the short Pb-O bonds. In the limit, the lone-pair plumbous ion can be written  $[\text{Pb}^{4+}\Psi^2]^{2+}$  with minimum Pb-O bond distance approaching  $\text{Pb}^{4+}\text{-O}$  2.18 Å (the mean for the  $\text{PbO}_2$  structures) for the side with bond pairs.

Both Pb coordinations are very irregular (Fig. 4). This is understandable considering that most of the surrounding O atoms are contained in the rigid three-dimensional framework

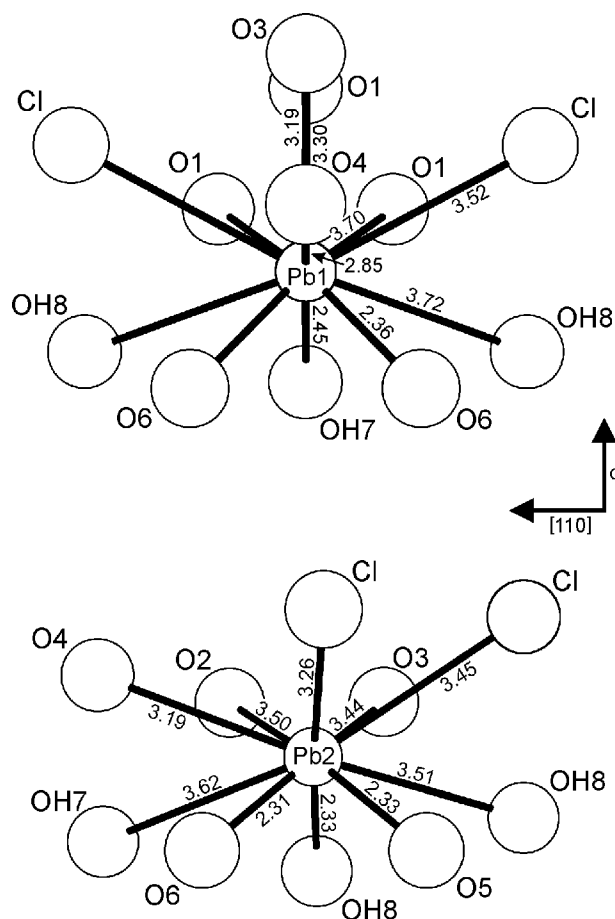


FIGURE 4. Pb coordinations in philolithite. The orientations are the same as for those shown in Figure 2.

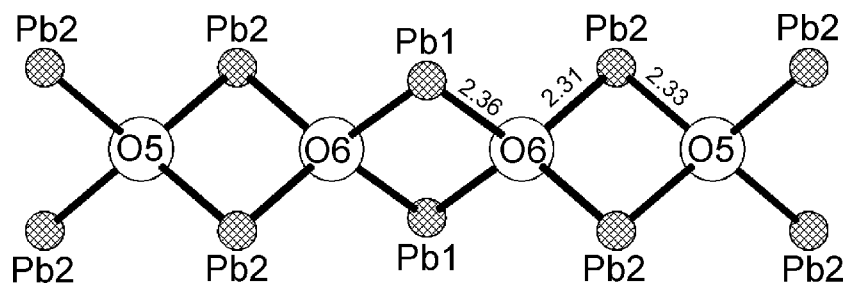


FIGURE 5. The chains of continuous Pb1, Pb2, O5, O6 links which run parallel to  $[110]$  and  $[\bar{1}10]$ .

formed by the other polyhedra and the positions of these O atoms are largely determined by their roles in the framework. Interestingly, the non-framework O atoms, O5 and O6, participate in the shortest Pb-O bonds, 2.31 to 2.36 Å. These O atoms are each surrounded by four Pb atoms in approximately tetrahedral configurations resulting in chains (Fig. 5) running parallel to  $[110]$  and  $[\bar{1}10]$ .

### Hydrogen bonding

Based upon bond valence considerations, the O atoms of the shared octahedral edges, OH7 and OH8, are presumed to correspond to OH groups (Table 5). Geometry and bond valence considerations suggest the hydrogen bonds OH7-H...O4 (2.68 Å) and OH8-H...Cl (3.20 Å). These are shown as thick dashed lines in Figure 2.

### DISCUSSION: THE STRUCTURE AS A CLOSEST-PACKED TRELLIS

The aforementioned open framework (less the  $\text{CO}_3$  groups) can be viewed as a cubic closest-packed trellis. Such a treatment deserves detailed explanation and analysis because of its novelty and far-reaching implications. To clarify this discussion, we will begin with a brief review of definitions and procedures. Despite the vast number of references to closest packings in the literature, surprisingly little systematics appears in compendia or books. This is amplified by the rich store of geometric and trigonometric relations found in closest-packed systems.

### Structure representation

In a series of articles, Moore (1994, 1995a, 1995b, 1996) outlined principles, proofs, and derivations of anionic closest-packings. The densest arrangement of equal and hard spheres remains a famous mathematical problem to this day (Cipra 1991).

A typical representation of closest-packing begins with the net  $\{3^6\}$ , composed of regular triangles  $\{3\}$ , six (= connectivity) of which meet at a common vertex. The nodal points of the net define the centroids of the disks which are the equatorial planes of equal and hard spheres. The perpendicular bisectors of the connected centroids provide the dual net (or Dirichlet domain),  $\{6^3\}$ . In this sense, the disks can also be considered as tangential to the midpoints of the hexagonal edges of  $\{6^3\}$ .

From constructed sheets of spheres based on  $\{3^6\}$  or  $\{6^3\}$ , successive sheets are stacked to minimize layer separation, H

(the distance between the planes containing the centroids of the spheres in successive sheets). This layer separation can be easily derived and corresponds to a sphere above and tangential to three spheres below (the "dimples"), specifically  $H = 2R\sqrt{2}/\sqrt{3}$ , where  $R$  is the radius of the sphere. The efficiency of packing ( $V_E$ ), that is the closest-packing volume of spheres divided by the total volume, is given by  $V_E = \pi/3\sqrt{2} = 0.7406+$  (or 74+% space filled).

If centroids of anions are connected together to give the polyhedral representation, two kinds of voids occur in closest-packings of anions ( $\emptyset$ ): regular octahedra (M) and regular tetrahedra (T); and they occur in the limit M:T: $\emptyset = 1:2:1$  or  $MT_2\emptyset$ . All closest-packed structures must be contained within this limit. The geometrical properties of octahedra and tetrahedra can form the basis for many derivations of dimensional properties in closest-packings, some of them surprisingly daunting. Examples include, the  $\emptyset$ -T- $\emptyset$  angle of the regular tetrahedron,  $\arccos(-1/3) = 109^\circ 28'$ , and the location of the centroid of a regular tetrahedron  $1/4$  of the way between a face and the opposing vertex. Such derivations are rarely encountered in texts. We advise the reader to derive or prove these relations.

Representation of structures in terms of closest-packings can take many forms. In particular, the linkage of bonds between cations (M, T) and anions ( $\emptyset$ ), often called a spoke diagram; the void fillings over available M and T; and the polyhedral representation. The polyhedra in general are called *Pauling polyhedra* and represent the connections of the coordinating anionic centroids about cations. The polyhedral representation as linkages is probably the easiest of visual access and the one we prefer to exploit.

The conventional closest-packing of spheres as the densest possible packing is called the *Kepler conjecture*, as the Lutheran mystic-astronomer-mathematician Johannes Kepler (1571–1630) was the first to derive it, but not formally prove it (Field 1988; Cipra 1991). As Nature seems to exploit the Kepler conjecture in so many ways and under so many circumstances, it is tempting to say that the conjecture may well be a principle or even a law.

As the conjecture begins with  $\{3^6\}$  or  $\{6^3\}$  in the plane and proceeds by extension, such structures can be conceived as *layered*, that is [anion ( $\emptyset$ ) boundary] – [cation (M, T) fillings] – [anion ( $\emptyset$ ) boundary]. In this sense, layers of two distinct structures may be *epitaxial* through matchings of a common two-sided plane group in the structures or through a twin boundary. This is a means of relating structure types to each other through common layers.

In addition, with respect to a fixed layer B and its normal stacking vector  $t^*$ , a successive layer can fit according to layer A or layer C. The two possible adjacencies are ABA (=h) and ABC (=c), called hexagonal and cubic sequences, respectively. Thus, closest-packed structures can be hexagonal ( $\cdot hh \cdot$ ), cubic ( $\cdot ccc \cdot$ ), or any one of the infinitely many possible mixed layers involving both h and c.

In this study, we will exploit the polyhedral representation and projection along  $t^*$  parallel to one of any four possible T- $\emptyset$  bonds in cubic closest-packing. For the purpose of counting, the *orthohexagonal unit* (Fig. 6) will be exploited. It includes two nodes or two  $\emptyset$  anions.

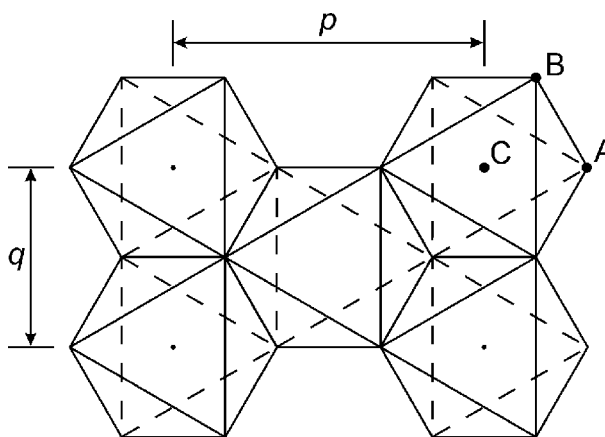
### The closest-packed trellis

Writing complete filling of anions  $\emptyset$  for M, T, and  $\emptyset$  occupied sites as  $\emptyset_n$ , then for  $\square_m\emptyset_{n-m}$  with  $m$  vacancies, the system may still be connected and can be conceived as an ordered subset of  $M_nT_{2n}\emptyset_n$ . Note that M and T populations are dependent on  $\square_m\emptyset_{n-m}$  populations. The linkage of M and T over partly filled  $\square_m\emptyset_{n-m}$  is called a *trellis*. This term must be invoked because closest-packings are usually meant to include fully populated  $\emptyset$ , the M and T populations being arbitrary.

To demonstrate that philolithite's structure includes a closest-packed trellis, a transformation is required. This gives  $a' = [112] = 30.88$ ,  $b' = [\bar{1}10] = 17.86$ ,  $c' = t^* = [\bar{1}\bar{1}1] = 21.89$  Å,  $\beta' = 90^\circ 06'$  (primes denote transformed cell). The matrix and the order of its determinant are  $[112/\bar{1}10/\bar{1}\bar{1}1]$ ,  $|A| = 6$ . It corresponds to 3 ( $\cdot ccc \cdot$ ) along  $c'$ , a nine-layer repeat based on cubic closest-packing. Evidently, the trellis in the transformed cell requires  $6p \times 6q \times 9r = 324$  orthohexagonal units (where  $p$ ,  $q$ , and  $r$  refer to the three vectors defining the orthogonal unit; see Fig. 6), or  $324 \times 2 = 648$  spheres with respect to the orthohexagonal unit.

The anion species which contribute to the closest-packing (and their cell multiplicities and point symmetries) include O1 ( $\times 8, m$ ), O2 ( $\times 8, m$ ), O3 ( $\times 8, m$ ), OH7 ( $\times 8, m$ ), OH8 ( $\times 16, 1$ ) or 48 anions. For the transformed cell, this is  $48 \times 6 = 288$  spheres. The percentage occupancy of closest-packed anion slots is evidently  $288/648 = 44.44\%$  anion occupancy. In other words, more than half the possible anion slots are empty, a quite open structure indeed.

Likewise, the associated cations in the trellis can be enumerated. They are M1 ( $\times 2, \bar{4}2m$ ), S ( $\times 2, \bar{4}2m$ ), M2 ( $\times 4, 2/m$ ), M3 ( $\times 8, m$ ). The generalized stoichiometry for the trellis in the transformed cell is  $M_{12}T_4\emptyset_{48}$ . The three-dimensional edifice has composition  $[^{60}(\text{Mn}, \text{Mg})_{12}^{2+} \text{ }^{14}(\text{SO}_4)_2 \text{ }^{14}(\text{Mn}^{2+} \text{O}_4)_2 \text{ }^6\text{O}_8 (\text{OH})_{24}]^{32}$ . It is constructed from linear (*trans*-) edge-sharing chains with  $6M'$  in the repeat along  $b' = [\bar{1}10]$  ( $b'/6 = 3.24$  Å) and equivalent edge-chains along  $[102]' = [110]$  which form in this orientation descending "staircases" of octahedra (see Fig. 7 which presents the trellis component). Note that the  $\text{MnO}_4$  and  $\text{SO}_4$



**FIGURE 6.** The orthohexagonal unit which can be formed on an AB slab.  $p = \sqrt{3} \cdot l$ ,  $q = l$ ,  $r = \sqrt{2}/\sqrt{3} \cdot l$ . Note  $r$  is the interlayer separation  $h$ .  $l$  is the M-M' (or  $\emptyset$ - $\emptyset'$ ) separation or  $l = 2 \times$  radius of a sphere.

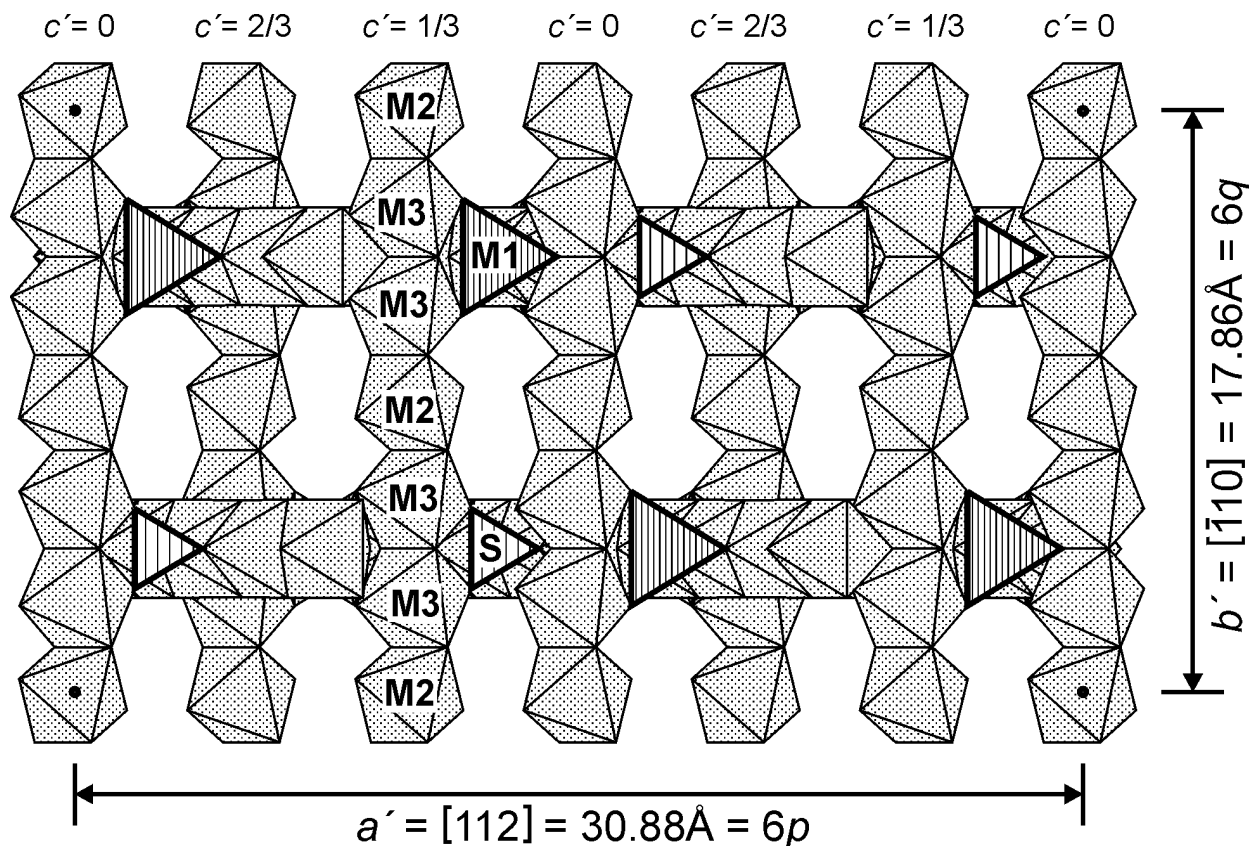


FIGURE 7. The trellis component of the crystal structure, which is made up of linked octahedra (M) and tetrahedra (T; thickly outlined) to give  $M_{12}T_4O_{48}$ , viewed along  $c'$ ,  $[111]$ . The heights along  $c'$  of the octahedral chains parallel to  $b'$  are shown.

tetrahedra weld the two chain orientations together at  $(\bar{4}2m)$ .

We regard the trellis framework as the fundamental unit for the structure. The structural principle behind philolithite's trellis is not complicated (staurolite has a similar arrangement, Hawthorne et al. 1993). Distortions within the trellis are largely a consequence of disparity in sizes of the  $SO_4$  and  $MnO_4$  tetrahedra. Another open structure of even greater complexity is betpakdalite,  $a' = 11.10$ ,  $b' = 19.44$ ,  $c' = 22.83$  Å,  $\alpha' = 91.70^\circ$ ,  $2[Mo_{32}^{6+}Fe_{12}^{3+}As_8^{5+}O_{148}]^{28-}$ , ten-layer  $2(-hcchc-)$  with percentage anion occupancy 46.25% (Moore 1992).

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