

## The crystal structure of cianciulliite, $\text{Mn}(\text{Mg},\text{Mn})_2\text{Zn}_2(\text{OH})_{10}\cdot 2\text{--}4\text{H}_2\text{O}$

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### ABSTRACT

The new species cianciulliite,  $\text{Mn}(\text{Mg},\text{Mn})_2\text{Zn}_2(\text{OH})_{10}\cdot 2\text{--}4\text{H}_2\text{O}$ , is monoclinic,  $C2/m$ , with  $a = 15.405(3)$ ,  $b = 6.344(1)$ ,  $c = 5.562(2)$  Å,  $\beta = 101.23(2)^\circ$ ,  $V = 533.2$  Å<sup>3</sup>, and  $Z = 2$ . The crystal structure was solved by direct methods and refined to  $R = 4.0\%$  using 675 observed X-ray diffractions. Solution of the structure was essential in determining the correct chemical composition of cianciulliite.

The atomic arrangement consists of two discrete (100) layers, a brucite-type layer and an  $\text{H}_2\text{O}$  layer. The brucite-type layer is formed of Mn and Mg octahedra, with the octahedral holes capped by  $\text{ZnO}_4$  tetrahedra. The apical OH of the Zn tetrahedra are H bonded to the  $\text{H}_2\text{O}$  layer. The  $\text{H}_2\text{O}$  layer readily loses  $\text{H}_2\text{O}$  during microprobe and X-ray analysis.

### INTRODUCTION

Cianciulliite, a new mineral species from Franklin, New Jersey, has been described by Dunn et al. (1991). The crystal structure determination of cianciulliite was begun knowing the amounts of the major cations Mn, Mg, and Zn, but the electron microprobe analysis totaled only 68 wt%. The valence state of Mn, the amounts of OH and  $\text{H}_2\text{O}$ , and the number of formula units per unit cell were determined by crystal structure analysis. The success of this method as a chemical analytical technique is described in detail by Hawthorne and Grice (1990).

### EXPERIMENTAL DETAILS

A thin cleavage fragment of cianciulliite with dimensions  $0.125 \times 0.125 \times 0.025$  mm was chosen from holotype material (CMN no. 56469) for the data collection. Intensity data were measured on an Enraf Nonius CAD-4 single-crystal diffractometer operated at 52 kV and 26 mA with graphite-monochromated  $\text{MoK}\alpha$  radiation. Data measurement and structure solution were performed using the NRCVAX package of computer programs (Gabe et al., 1985). A set of 59 reflections permuted four ways,  $\pm h$  at  $\pm 2\theta$ , was used to refine the cell parameters to  $a = 15.405(3)$ ,  $b = 6.344(1)$ ,  $c = 5.562(2)$  Å and  $\beta = 101.23(2)^\circ$ . A full sphere of data was collected to  $2\theta = 60^\circ$  assuming a C-centered lattice. The intensities were corrected for Lorentz and polarization effects, and a Gaussian absorption correction ( $\mu = 66.6$  cm<sup>-1</sup> for  $\text{MoK}\alpha$  radiation) was applied. Of the 3854 measured intensities, 835 are independent and 675 of these are observed [ $F > 5.0\sigma(F)$ ]. It is significant to the structure refinement that over the 6 d duration of data measurement, two of the standard reflections, 040 and 002, maintained the same intensity within  $\pm 1\%$  but the third standard reflection, 800, decreased in intensity by 12%.

### CRYSTAL STRUCTURE ANALYSIS

The crystal structure was solved by direct methods and difference Fourier maps in space group  $C2/m$ . Scattering curves for neutral atoms and anomalous dispersion were taken from Cromer and Mann (1968) and Cromer and Liberman (1970), respectively. With all the cations and O atoms properly identified and placed, the model refined with isotropic temperature factors to a residual index of  $R = 8.8\%$ . Upon conversion to anisotropic temperature factors, the model converged to a final residual index of  $R = 4.0\%$ . The O5 atomic position, occupied by an  $\text{H}_2\text{O}$  molecule, refined with the most reasonable temperature factors when it was located at a disordered position of half occupancy just off the mirror plane; thus it was released from the special position.

Because of the rather poor quality of crystals and their subsequent decrepitation on exposure to X-rays, the intensity data were not of sufficient quality to locate H atoms. In the final stages of refinement ( $R = 4.0\%$ ),  $\Delta F$  maps gave locations of weak peaks near O2 and O3 sites and even weaker ones near O1 and O4, but we are not confident that these are truly due to H atoms. On the basis of the constants of Brown (1981), bond-valence sums for each site are Mn 2.04, (Mg,Mn) 1.99, Zn 1.89, O1 1.05, O2 1.15, O3 0.49, O4 1.06, O5 0.00 vu. This gives rise to the structural formula  $\text{Mn}(\text{Mg},\text{Mn})_2\text{Zn}_2(\text{OH})_{10}\cdot 2\text{H}_2\text{O}$  with  $Z = 2$ .

Table 1 contains the final positional and thermal-vibration parameters. Selected interatomic distances and angles are presented in Table 2. The observed and calculated structure factors, Table 3, have been deposited.<sup>1</sup>

<sup>1</sup> A listing of the observed and calculated structure factors, Table 3, may be ordered as Document AM-91-470 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 1. Positional coordinates and thermal parameters ( $\text{\AA}^2$ ) in cianciulliite

	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
Mn	0	0	0	2.09(9)	0.87(9)	1.02(9)	0	0.43(6)	0	1.31(6)
Mg	0	0.2536(2)	1/2	2.10(8)	0.70(7)	1.00(7)	0	0.53(5)	0	1.22(4)
Zn	0.6187(1)	0	0.0705(2)	2.00(5)	1.05(4)	1.12(4)	0	0.34(3)	0	1.39(3)
O1	0.0671(4)	0	0.371(1)	2.0(3)	1.8(3)	1.9(3)	0	0.4(2)	0	1.6(2)
O2	0.5777(4)	0	0.385(1)	2.4(3)	1.1(2)	1.0(2)	0	0.7(2)	0	1.5(2)
O3	0.7485(5)	0	0.166(1)	2.4(3)	6.4(6)	1.7(3)	0	0.6(2)	0	3.4(2)
O4	0.4175(2)	0.2538(6)	0.1282(7)	2.0(2)	1.0(2)	1.3(2)	-0.4(1)	0.2(1)	-0.3(1)	1.4(1)
O5	0.2479(6)	0.064(1)	0.315(1)	3.2(4)	3.3(5)	1.8(4)	0.3(3)	0.8(3)	0.1(4)	2.7(3)

Note: Temperature factors are of the form  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$ . Estimated standard deviations are in parentheses.

### DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The most striking feature of the cianciulliite structure is the layering parallel to (100), the dominant cleavage plane (Fig. 1). The H<sub>2</sub>O layers (O5 is the H<sub>2</sub>O molecule) are interleaved with cation layers that consist of Mn and Mg in octahedral coordination and Zn in tetrahedral coordination.

The water (O5) layers are H bonded to the cation layers through O3, with an O3-O5 distance of 2.72 Å (Table 2). The H<sub>2</sub>O molecules were close to a special position on the mirror plane, but if constrained to refine on this plane (at  $y = 0$ ) the residual index did not refine below  $R = 4.5\%$  and the temperature factor across the mirror plane ( $U_{22}$ ) was approximately ten times larger than those in the other two directions. For these reasons the occupant of the H<sub>2</sub>O site was allowed to refine in a general position just off the mirror plane, with half occupancy. This model with disordered H<sub>2</sub>O gave a better residual index,  $R = 4.0\%$ , and more consistent anisotropic temperature factors (Table 1). The fact that the H<sub>2</sub>O molecule occupies a general position is significant because a small shift from its present position (for example, a 1.2 Å shift to a general

position at 0.25,0.25,0.25) would yield H<sub>2</sub>O-H<sub>2</sub>O distances that would allow eight H<sub>2</sub>O molecules per unit cell rather than the four observed in this experiment. It is very possible that the full cell formula for fully hydrated cianciulliite is  $\text{Mn}_2(\text{Mg},\text{Mn})_4\text{Zn}_4(\text{OH})_{20}\cdot 8\text{H}_2\text{O}$  and that one-half of the weakly bonded H<sub>2</sub>O molecules are lost under laboratory conditions. In support of this proposed formula is the observed volatilization of H<sub>2</sub>O during electron microprobe analysis (Dunn et al., 1991) and the collapse of the structure along the *a* axis during X-ray analysis.

The cation layer (Fig. 2) consists of a sheet of edge-sharing octahedra with one quarter of the octahedral sites vacant. The octahedral holes have an orthogonal arrangement and are capped on either side by Zn in tetrahedral coordination. All of the cation ligands are OH, and it is probable that the octahedral holes are not void but contain H atoms bonded to O2 and O4.

There are several manganese oxide minerals with layered structures, notably birnessite, busserite, and manganoite. The phyllophanes have been studied in great detail as they are a major component of marine nodules. The most recent reviews by Burns et al. (1983) and Giovanoli (1985) contain many references on this topic. The

TABLE 2. Selected interatomic distances (Å) and angles (°) in cianciulliite

Mn octahedron			Mg octahedron		
Mn-O1	2.118(5) × 2		Mg-O1	2.113(4) × 2	
Mn-O4	2.218(4) × 4		Mg-O2	2.141(4) × 2	
Mean	2.184		Mg-O4	2.207(3) × 2	
		83.6(1) × 4	Mean	2.154	
O1-O4	2.891(5)	96.4(1) × 4	O1-O1	2.740(12)	80.8(3)
O1-O4	3.232(5)	90.4(2) × 2	O1-O2	3.176(6)	96.6(2) × 2
O4-O4	3.148(5)	89.6(2) × 2	O1-O4	3.164(6)	94.2(2) × 2
O4-O4	3.124(5)	90.0	O1-O4	2.892(6)	84.0(2) × 2
Mean	3.086		O2-O2	2.926(13)	86.2(3)
			O2-O4	3.138(6)	92.4(2) × 2
			O2-O4	3.059(6)	89.4(2) × 2
			Mean	3.044	90.0
Zn tetrahedron			O5 distances		
Zn-O2	1.973(6)		O5-O3	2.72(1)	
Zn-O3	1.967(7)		O5-O3	2.89(1)	
Zn-O4	1.970(4) × 2		O5-O3	2.90(1)	
Mean	1.970		O5-O2	2.90(1)	
O2-O3	3.108(10)	104.1(3)	O5-O1	2.89(1)	
O2-O4	3.291(9)	113.1(1) × 2	O5-Zn	3.27(1)	
O3-O4	3.192(7)	108.3(2) × 2			
O4-O4	3.220(8)	109.5(2)			
Mean	3.216	109.4			

Note: Estimated standard deviations are in parentheses.

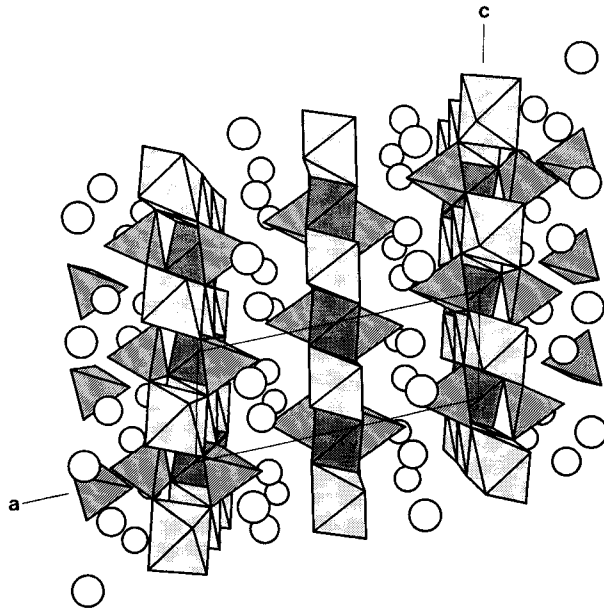


Fig. 1. A perspective view down the *b* axis of the cianciulliite structure. The Mn octahedra are darkly shaded, (Mg,Mn) octahedra are lightly shaded, Zn tetrahedra are ruled, and H<sub>2</sub>O molecules (O5) are large open circles. The lower face of the unit cell is outlined.

minerals that have the closest chemical relationship to cianciulliite are chalcophanite, ZnMn<sub>3</sub>O<sub>7</sub>·3H<sub>2</sub>O, and woodruffite, (Zn,Mn<sup>2+</sup>)Mn<sup>3+</sup>O<sub>7</sub>·1–2H<sub>2</sub>O, but only the former is closely related structurally.

The crystal structure of woodruffite has not been determined, but it is probably isostructural with todorokite, which has recently been refined by Post and Bish (1988). Todorokite has a tunnel structure that does not resemble that of cianciulliite. The chalcophanite structure (Post and Appleman, 1988) consists of layers with the sequence Mn-O-Zn-H<sub>2</sub>O-Zn-O-Mn in the direction perpendicular to the layering. This closely resembles the layering sequence of cianciulliite of (Mn,Mg)-OH-Zn-(OH,H<sub>2</sub>O)-Zn-OH-(Mn,Mg). Similar to cianciulliite, the Mn octahedral layer of chalcophanite has a hexagonal net, but unlike cianciulliite it has fewer octahedral holes, with only one in seven of the octahedral sites vacant. The chalcophanite octahedral layer could be regarded as intermediate between that of pyrochroite, Mn(OH)<sub>2</sub>, which has a fully occupied brucite-like octahedral layer, and that of cianciulliite, with octahedral vacancies at one quarter of the cation sites. The octahedral holes are capped by Zn in cianciulliite and chalcophanite, but the Zn coordination in each differs. In cianciulliite, Zn is tetrahedrally coordinated by OH, whereas in chalcophanite Zn has sixfold coordination with three O atoms shared with the Mn octahedra (bond lengths 1.86–1.97 Å) and three H<sub>2</sub>O molecules on the other side that form the H<sub>2</sub>O layer (bond lengths 2.14 Å) (Post and Appleman, 1988). The increased coordination of Zn in chalcophanite relative to

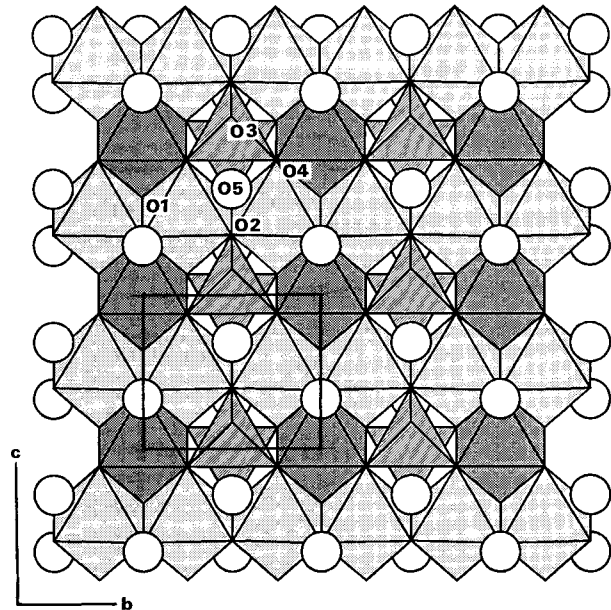


Fig. 2. A projection of the cianciulliite structure on (100). Mn octahedra are darkly shaded, (Mg,Mn) octahedra are lightly shaded, Zn tetrahedra are ruled, and H<sub>2</sub>O molecules (O5) are large open circles. The unit cell is outlined.

that of cianciulliite is affected by lowering the Lewis base strength of the three O atoms shared by the octahedral layer. This is because these three O atoms are part of the Mn<sup>4+</sup> octahedra; Mn<sup>4+</sup> has a much higher Lewis acid strength than Mg and Mn<sup>2+</sup>, which occupy these octahedra in cianciulliite.

The H<sub>2</sub>O molecular layer is only weakly H bonded in cianciulliite and hence partially lost in sample preparation and analytical procedures. The comparison with the chalcophanite structure suggests a mechanism for the higher hydrate of cianciulliite with increased numbers of H<sub>2</sub>O molecules H bonded to the Zn tetrahedron. Thus we suggest the general formula Mn(Mg,Mn)<sub>2</sub>Zn<sub>2</sub>(OH)<sub>10</sub>·2–4H<sub>2</sub>O for cianciulliite. The variable H<sub>2</sub>O content expresses the range expected for the mineral under normal laboratory conditions.

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