

## Additional data on the crystal structure of montgomeryite

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### Abstract

An independent structural study on montgomeryite confirms the general features previously reported by Moore and Araki (1974). However the presence of several weak  $h0l$  reflections with  $l$  odd shows that the symmetry of the mineral is actually lower than  $C2/c$ . An attempt to explain the disorder around the partially occupied  $Mg^{2+}$  site by degrading the local symmetry leads to a completely ordered atomic arrangement in the  $C2$  space group and affords a reasonable improvement in the coordination around this ion.

### Introduction

Our work on the crystal structure of montgomeryite was just completed and the manuscript ready for publication, when we learned of the results of the structure determination by Moore and Araki (1974) (hereafter MA). The chemical formula of the mineral proposed by Gonyer (in Larsen, 1940),  $Ca_4Al_5(PO_4)_6(OH)_5 \cdot 11H_2O$ , was revised by MA to  $Ca_4Al_4Mg(PO_4)_6(OH)_4 \cdot 12H_2O$ . When our present study was completed, a laser microprobe analysis of a small crystal in our sample also revealed the presence of magnesium. Our determination confirms the general features of the structure as reported, but some minor differences as well as the independence of the two determinations warrant publication of a condensation of our results.

### Experimental, structure determination and refinement

A well formed lath-shaped crystal of montgomeryite from Fairfield, Utah, obtained through the courtesy of Arthur Montgomery, was mounted on the goniometer head of a Philips PW 1100 automatic diffractometer equipped with graphite monochromator and molybdenum tube. The instrumental lattice constants, determined by the least squares method applied to the values of  $\omega$ ,  $\chi$  and  $\phi$  arcs for reflections with  $2\theta$  of about  $34^\circ$ , are:

$$a = 10.004, \quad b = 24.083, \quad c = 6.235 \text{ \AA}, \quad \beta = 91^\circ 36'.$$

The comparison of intensities of related reflections and systematic extinctions with  $h+k = 2n+1$  indicated monoclinic symmetry and  $C$ -centered lattice, but the previous assignment to the space group  $C2/c$

remained in doubt because of the presence of some very weak  $h0l$  reflections with  $l$  odd. These reflections were present on Weissenberg photographs previously taken with  $CuK\alpha$  radiation, and were also exhibited by a second crystal tested on the diffractometer. These facts suggest a lower symmetry than  $C2/c$ . However, since the "forbidden" reflections with an intensity above the background are very few (only 33 out of 65  $h0l$  reflections with  $l$  odd measured) and their intensities are very low, they were at first ignored and the apparent  $C2/c$  symmetry was assumed to be correct at the beginning of the structural determination.

2195 independent reflections in the range  $6^\circ \leq 2\theta \leq 60^\circ$  were measured with the  $\omega/2\theta$  scan technique. Of these 171 were ignored since their intensities were within background error.

The structure was solved by the symbolic addition procedure for centrosymmetric space groups, using the program LSAM (Germain, Main, and Woolfson, 1971), applied to the 287  $E$ 's  $\geq 1.5$ . A Fourier map computed with 284  $E$ 's from the set of signs with the highest figures of merit revealed all non-oxygen atoms in the asymmetric unit. The structure was refined by successive Fourier syntheses to an  $R$  value of 0.18.

At this stage we had ascribed a residual electronic density on the two-fold axes in approximate octahedral coordination by oxygens to the presence of  $X$  ions in the asymmetric unit. Since Gonyer's analysis revealed no cations except Al and Ca, these  $X$  ions were assumed to be Al. The resulting total cell content was  $Ca_8Al_{12}(PO_4)_{12}(OH)_{16} \cdot 16H_2O$ . This trial structure was refined in the  $C2/c$  space group by the least-squares method. In three cycles using isotropic

individual thermal parameters, the  $R$  index dropped to 0.11. At this stage it appeared clear that the aluminum ion labelled as Al(3) on the two fold axis at the  $X$  site, having a high thermal parameter, exhibited only partial occupancy. A cycle of refinement was then performed allowing the occupancy of Al(3) to vary: the resulting occupancy converged to 0.50, while the  $B$  parameter assumed a quite acceptable value.

Anisotropic thermal parameters were then assigned and refined for all atoms but OW(3) and Al(3) (whose occupancy was fixed as 50 percent). Ignoring the "forbidden"  $h0l$  reflections, in two cycles the  $R$  index dropped to 0.061 for 1991 observed reflections.

A Fourier difference map computed at this stage revealed that the strongest maxima lie in the zone around Al(3) and that OW(3), which exhibits a high isotropic thermal parameter, revealed a strong anisotropy. This fact and the large Al(3)-OW(3) distance (2.278Å) suggests that the apparent thermal anisotropy is probably due to a splitting of OW(3) in two positions OW(3a) and OW(3b), alternately occupied when Al(3) is present or absent. When Al(3) is present, OW(3) would occupy the positions nearer to the cation, normalizing the Al-O distances in the octahedron. An attempt was then made to refine the structure, splitting OW(3) in these two positions, each one with an occupancy of 50 percent. This cycle lowered the  $R$  index to 0.056; the split OW(3) molecule afforded a more acceptable thermal parameter and Al(3)-O distances were improved. The results of the refinement are fairly satisfactory, but the "average" structure, obtained by equally distributing Al(3) on two positions related by the  $c$  glide symmetry operation and by splitting OW(3) from a statistical point of view, fails to explain the presence of the weak  $h0l$  reflections with  $l$  odd.

At this stage, in order to justify the weak  $h0l$  reflections with  $l$  odd, an attempt was made to refine the structure assuming an ordered model in the space group  $C2$ ; this group is the most symmetrical subgroup of  $C2/c$  that is consistent with the observed extinctions. High correlations between positional and thermal parameters of related atoms revealed that a refinement of all parameters in space group  $C2$  was impossible. Therefore in the next attempt we fixed the structural parameters, with the exception of the Al(3) coordination octahedron, and destroyed the  $c$ -glide symmetry with respect to Al(3) by assuming that this octahedron is present only in one of the two positions related by the glide-plane. The refinement was restricted to Al(3) and to the two non-equivalent atoms

corresponding to OW(3) in the centric space group. The final  $R$  index for 2024 observed reflections is 0.053. Notwithstanding the impossibility of testing the two hypotheses on the basis of statistical considerations derived from equivalent refinements performed in two different space groups, the ordered model in the  $C2$  space group has to be considered a better model for the actual structure of the mineral. Very small deviations from  $C2/c$  symmetry must involve all the atoms in the structure but only the region around Al(3) accounts for the lower symmetry described herein.

The ordered atomic arrangement of montgomeryite is featured in Figure 1. For sake of comparison, the origin is still coincident with that chosen by MA in the  $C2/c$  space group.

Atomic coordinates and thermal parameters, resulting from both refinements, are listed in Table 1. In this table the  $X$  position is indicated as Mg rather than Al(3). Indeed the chemical analysis of MA with a Mg content corresponding to two ions per unit cell as well as the interatomic distances suggest that  $Mg^{2+}$  ions are preferentially located in the  $X$  position. However, the substitution of  $Al^{3+}$  for  $Mg^{2+}$  in the structure analysis does not vitiate the results of the refinement, because both ions have similar scattering curves.

## Results and discussion

Our structure for montgomeryite closely resembles that of MA; thus further discussion seems unnecessary. The major difference lies in our interpretation of the atomic arrangement around the Mg ion according to an ordered model in the  $C2$  space group. This model accounts for the weak  $h0l$  reflections with  $l$  odd and with the magnesium content in the cell. It also yields a significant decrease in the

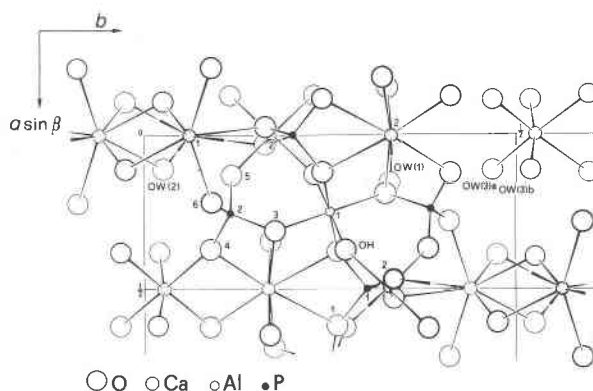


FIG. 1. Montgomeryite structure projected along the  $c$  axis.

TABLE 1. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors (after Hamilton, 1959)

Atom	x	y	z	B(Å <sup>2</sup> )
Ca(1)	0	.06132(6)	1/4	0.97
Ca(2)	0	.33082(5)	1/4	0.97
Al(1)	1/4	1/4	0	0.48
Al(2)	0	.17177(7)	-1/4	0.46
P(1)	1/2	.29949(6)	-1/4	0.46
P(2)	.25851(10)	.11538(4)	-.04081(16)	0.59
O(1)	.61740(27)	.26034(13)	.70925(47)	0.88
O(2)	.47001(29)	.33638(13)	.55578(47)	1.26
O(3)	.30933(30)	.17528(12)	.01354(51)	0.84
O(4)	.37484(31)	.08760(13)	-.15171(52)	0.98
O(5)	.13698(29)	.11774(13)	-.20051(53)	0.97
O(6)	.21850(36)	.08628(15)	.16276(57)	1.55
OH	.37062(28)	.27169(12)	.21882(49)	0.60
OW(1)	.16222(37)	.32941(18)	.53004(62)	1.99
OW(2)	.11263(32)	.02580(14)	.58142(55)	1.26
a) C2/c symmetry; occupancy factors equal to 0.5.				
Mg	0	.52867(17)	-1/4	1.16*
OW(3)(a)	.11621(71)	.46807(31)	.61315(116)	2.70*
OW(3)(b)	.12130(71)	.51881(30)	.02617(112)	2.54*
b) C2 symmetry; equivalent positions: x, y, z; -x, y, 1/2-z; 1/2+x, 1/2+y, z; 1/2-x, 1/2+y, 1/2-z.				
Mg	0	.52890	-1/4	1.39*
OW(3)(a)	.11611	.46729	.60002	1.76*
OW(3)(b)	.12128	.51910	.04472	1.30*

\* These atoms were refined isotropically.

(Standard Deviations in Parentheses)

distortion of the Mg coordination octahedra and results in a slightly different arrangement of the hydrogen bonds.

Accepting this ordered model, each magnesium ion coordinates to two O(4) atoms at 1.996 Å, two

OW(3a) molecules at 2.186 Å and two OW(3b) molecules at 2.118 Å. These water molecules are involved in some relatively strong hydrogen bonds: OW(3a) ... O(6) = 2.54 Å and OW(3b) ... O(4) = 2.65 Å. Two other interactions can be ascribed to hydrogen bonds: OW(3b)-OW(2), 2.80 Å, and OW(3a)-OW(2), 2.97 Å. In this model Mg octahedra are not linked together; the lack of edge-sharing Mg chains is a relevant feature in view of the classification of the mineral.

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