

Montgomeryite, $\text{Ca}_2\text{Mg}(\text{H}_2\text{O})_{12}[\text{Al}_4(\text{OH})_4(\text{PO}_4)_6]$: Its Crystal Structure and Relation to Vauxite, $\text{Fe}^{2+}_2(\text{H}_2\text{O})_4[\text{Al}_4(\text{OH})_4(\text{H}_2\text{O})_4(\text{PO}_4)_4] \cdot 4\text{H}_2\text{O}$

PAUL BRIAN MOORE, AND TAKAHARU ARAKI

Department of the Geophysical Sciences, The University of Chicago
Chicago, Illinois 60637

Abstract

Montgomeryite, $\text{Ca}_2\text{Mg}(\text{H}_2\text{O})_{12}[\text{Al}_4(\text{OH})_4(\text{PO}_4)_6]$, $Z = 2$, a 10.023(1), b 24.121(3), c 6.243(1) Å, β 91.55(1)°, space group $C2/c$, possesses chains of corner-linked Al–O octahedra which are topologically and geometrically equivalent to the chains in vauxite, $\text{Fe}^{2+}_2(\text{H}_2\text{O})_4[\text{Al}_4(\text{OH})_4(\text{H}_2\text{O})_4(\text{PO}_4)_4] \cdot 4\text{H}_2\text{O}$. The octahedra are linked by the (OH)⁻ ligands and are alternately in *cis*- and *trans*-configurations. The octahedral chain and associated tetrahedra can be written $[\text{Al}_4(\text{OH})_4(\text{PO}_4)_6]^{10-}$; for vauxite, it is $[\text{Al}_4(\text{OH})_4(\text{H}_2\text{O})_4(\text{PO}_4)_4]^{4-}$. These units are proposed to be underlying features of the two structures with the more weakly bonded cations intercalated in the remaining spaces. In montgomeryite, the (PO₄) tetrahedra bridge to equivalent chains along the *c*-axis, forming slabs parallel to {010}, which is the direction of perfect cleavage.

Average interatomic distances are ^{iv}P(1)–O 1.536 Å, ^{iv}P(2)–O 1.541 Å, ^{vi}Al(1)–O 1.894 Å, ^{vi}Al(2)–O 1.913 Å, ^{vi}Mg–O 2.144 Å, ^{viii}Ca(1)–O 2.553 Å, ^{viii}Ca(2)–O 2.460 Å. The Mg atoms are disordered and occupy only half of their available sites.

Introduction

Montgomeryite is one of several species of basic calcium aluminum phosphates which were described by Larsen (1940) in his classic study on the phosphate nodule paragenesis of Fairfield, Utah. It occurs with wardite, englishite, and gordonite which replace variscite in open seams and which in turn are followed by “pseudowavellite” (= crandallite) and a member of the apatite group. More recently, montgomeryite has been described by Moore (1964) as a very late mineral in mitridatite nodules from the Etta pegmatite, near Keystone, South Dakota.

Our interest in the systematic crystal chemistry of the basic aluminum and ferric phosphates prompted an X-ray investigation of the montgomeryite structure, fine crystals of which were kindly provided by its namesake, Mr. Arthur Montgomery.

Experimental

A broken single crystal measuring 0.17 mm along the *a*-axis, 0.06 mm along *b*, and 0.14 mm along *c* was prepared for a PICKER four-circle diffractometer. Data were collected using graphite monochromatized MoK α radiation, $2\theta_{\text{max}} = 60^\circ$, scan speed 2°/minute, with 20-second background mea-

surements on each side of the peak. An absorption correction for the crystal, approximated by eight bounding planes, was applied employing the Gaussian integral method described by Burnham (1966). A total of 2200 independent reflections were available for the ensuing analysis. Cell parameters, refined by a least-squares fit to diffraction measurements of a selected set of reflections, are provided in Table 1.

Structure Determination and Refinements

The Patterson synthesis, $P(uvw)$, revealed a linear concentration of prominent vectors at $0, v, 0$; $1/2, v, 0$; and $1/4, v, 1/4$; and suggested that most cations reside on the 2-fold rotor passing through $0, y, 1/4$ and that one cation resides on $1/4, 1/4, 0$.

The selected positions eventually labelled Al(1), Al(2), P(1), Ca(1) and Ca(2) provided sufficient input for a β -general synthesis, described by Ramachandran and Srinivasan (1970). This resulted in resolution of all non-hydrogen atoms. In addition to the expected electron densities, a weak density appeared at $0, 0.473, 1/4$. Two cycles of occupancy and coordinate parameter refinement revealed that this occupancy corresponded to about 5 electrons.

TABLE 1. Montgomeryite: Structure Cell Parameters

	1	2
a (Å)	10.023(1)	9.99(2)
b (Å)	24.121(3)	24.10(2)
c (Å)	6.2429(9)	6.25(5)
β	91.55(1)°	91.47°
space group	C2/c	C2/c
Z	2	2
formula unit	Ca ₄ Mg(H ₂ O) ₁₂ [Al ₄ (OH) ₄ (PO ₄) ₆]	Ca ₄ Al ₅ (PO ₄) ₆ (OH) ₅ ·11H ₂ O
density (calc) (gm cm ⁻³)	2.523	
sp. gr.		2.530(5)

1. This study; 2. Larsen (1940).

Two more cycles, utilizing correction for secondary extinction and $I(hkl) = \sigma(I)$ for unobserved reflections, afforded rapid convergence and a sharp electron density map. Full-matrix least-squares refinement, including all atomic coordinates and isotropic thermal vibration parameters for all 2200 reflections, led to $R(hkl) = \sum ||F_{obs} - F_{calc}|| / \sum |F_{obs}| = 0.097$; and $R = 0.058$ for the 1223 reflections which were greater than three times their background errors.

The scattering curves for Al³⁺, Ca²⁺, P⁰, O¹⁻ and Na¹⁺ were obtained from the analytical expressions of Cromer and Mann (1968) and included the anomalous dispersion terms for Al, Ca, and P. The final atomic coordinates and isotropic thermal vibration parameters appear in Table 2, and the structure factor data are provided in Table 3.

Chemical Formula: Revision of the Montgomeryite Composition

The small but real electron density at 0, 0.473, 1/4 must be accepted as a necessary part of the montgomeryite structure. Interatomic distance and angle calculations, as well as the polyhedral diagram discussed further on, suggested that this site is half-occupied by a Mg²⁺ cation. Accordingly, we obtained an electron probe analysis for Mg and found Mg = 2.17 percent by weight. We thank Dr. A. J. Irving for this analysis.

The unit formula, $Z = 2$, is Ca₄Mg(H₂O)₁₂[Al₄(OH)₄(PO₄)₆], which affords calculated Mg of 2.12 percent by weight. The analysis of Gonyer in Larsen (1940) does not report Mg²⁺; this might have been co-precipitated with the alumina in the wet chemical analysis. A revised formula for overite based on a probe analysis was recently reported by Moore (1974) who notes that nearly half the earlier reported Al₂O₃ for that mineral is actually MgO. Thus, in the Fairfield, Utah, paragenesis, at least three species—montgomeryite, overite, and gor-

donite—contain essential MgO which doubtless contributes to the complex phase relations of the paragenesis. This suggests that the formulae of the paragenetically related but poorly understood species, englishite and lehiite, should be treated with caution until new information comes to light.

We note the excellent agreement of the computed density based on the revised montgomeryite formula and cell data in Table 1 with the well-established specific gravity of the mineral by Larsen (1940).

Description of the Structure

The Polyhedral Diagram and its Interpretation

Montgomeryite possesses a rather complex crystal structure whose underlying feature is a chain of corner-linked Al-O octahedra (Fig. 1). These Al-O chains are linked along the *c*-direction to equivalent chains by [PO₄] tetrahedra. This results in a slab of P-O tetrahedra and Al-O octahedra oriented parallel to the {010} plane. Between these slabs, the larger [MgO₆] octahedra and [CaO₈] polyhedra occur. The Ca(2)-O polyhedra are tucked in close to each slab, with the outlying Mg-O and Ca(1)-O polyhedra bridging to symmetry equivalent slabs related by the *C*-centering. Since the Mg-O octahedra are only half-occupied on the average and since the larger Ca(1)-O polyhedra possess relatively weak bond strengths, the strongest bonds are largely concentrated in the slabs. Thus, montgomeryite possesses perfect {010} cleavage.

TABLE 2. Montgomeryite. Cell Multiplicities, Atom Coordinates, and Isotropic Thermal Vibration Parameters*

Atom	Multi- plicity	x	y	z	B(Å ²)
Ca(1)	4	0.0000	0.06115(6)	0.2500	1.35(3)
Ca(2)	4	.0000	.33098(6)	.2500	1.03(3)
Mg	2	.0000	.4708(2)	.2500	0.75(12)
Al(1)	4	.2500	.2500	.0000	0.79(3)
Al(2)	4	.0000	.17151(9)	-.2500	0.84(3)
P(1)	4	.5000	.29944(7)	-.2500	0.74(3)
P(2)	8	.2582(1)	.11548(5)	-.0405(2)	0.87(3)
O(1)	8	.6172(4)	.2604(2)	.7072(6)	1.13(6)
O(2)	8	.4693(4)	.3366(2)	.5548(6)	1.12(6)
O(3)	8	.3096(4)	.1749(2)	.0120(6)	1.06(6)
O(4)	8	.3754(4)	.0872(2)	-.1497(6)	1.24(6)
O(5)	8	.1362(4)	.1178(2)	-.2009(6)	1.24(6)
O(6)	8	.2184(4)	.0856(2)	.1620(7)	1.69(7)
OH	8	.3712(4)	.2715(2)	.2189(6)	0.88(5)
OW(1)	8	.1614(5)	.3301(2)	.5292(7)	2.11(7)
OW(2)	8	.1122(4)	.0261(2)	.5826(7)	1.59(6)
OW(3)	8	.1188(6)	.4731(2)	.5723(10)	3.69(11)

* Estimated standard errors in parentheses refer to the last digit.

The edge-sharing Mg–O octahedra form a chain parallel to the *c*-axis. Likewise, the Ca–O polyhedra share edges to form columns also running in this direction. Despite the complexity of the structure, we propose that the underlying structural principles—the Al–O octahedral chains—are relatively simple motifs and that the remaining large cations do not play a major role in the montgomeryite architecture.

Polyhedral Interatomic Distances

Of the average interatomic distances (Table 4), only the Mg–O average deviates significantly from typical values (2.07–2.09 Å) found in the structures of similar hydrated phosphates. We attribute this to the disordered and half-occupied character of that site. Table 4 provides a list of interatomic distances and angles: these values are arranged in increasing distances, and we note that the associated O–Me–O' angles also roughly increase in value.

Hydrogen Bonds and Electrostatic Valence Balances

The locations of possible hydrogen bonds were inferred from geometrical arguments. The potential

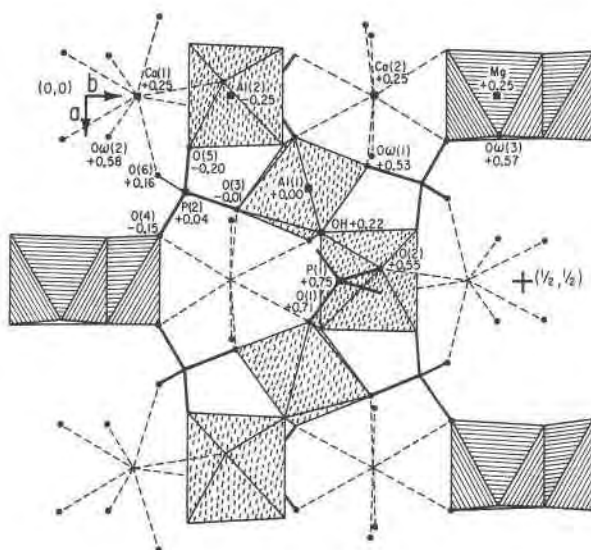


FIG. 1. Polyhedral diagram of montgomeryite down the Z^* -axis. The underlying Al–O octahedra are stippled, and the half-occupied Mg–O octahedra are ruled. The P–O bonds are shown as solid lines and the Ca–O bonds are dashed. Locations of atoms and their heights in fractional coordinates refer to Table 2.

TABLE 4. Montgomeryite. Polyhedral Interatomic Distances and Angles*
(Estimated standard errors in parentheses refer to the last digit)

Al–O Octahedra			P–O Tetrahedra			Mg–O Octahedron		
Al(1)			P(1)			Mg		
2 Al(1)	–OH ⁱ	1.877(5) Å	2 P(1)–O(1)	1.534(5)		2 Mg	–O(4) ⁱⁱⁱ	1.988(7)
2	–O(1)	1.898(5)	2	–O(2)	1.538(5)	2	–OW(3) ^v	2.133(8)
2	–O(3)	1.908(5)	average	1.536		2	–OW(3)	2.311(8)
average		1.894 Å				average		2.144
O–Me–O'			1 O(1)–O(1) ⁱ	2.423(7)	104.33	2 O(4) ⁱⁱⁱ –O(3) ^v	2.795(8)	85.33
2 O(3)	–O(1) ⁱ	2.592(7)	1 O(2)–O(2) ⁱ	2.498(7)	108.60	1 O(4) ⁱⁱⁱ –O(4) ⁱⁱⁱ	2.824(7)	90.51
2 O(3)	–OH ⁱⁱ	2.625(7)	2 O(1)–O(2)	2.531(7)	110.96	2 OW(3) ^v –OW(3)	2.838(8)	79.27
2 O(1) ⁱⁱⁱ	–OH	2.659(7)	2 O(1)–O(2) ⁱ	2.531(7)	110.96	2 OW(3)	–O(4) ⁱⁱⁱ	3.015(8)
2 O(1) ⁱ	–OH	2.679(7)	average	2.508	109.46	2 OW(3)	–O(4) ⁱⁱⁱ	3.131(8)
2 O(3)	–OH	2.727(7)				1 OW(3) ^{iv} –OW(3) ^v	3.298(8)	101.27
2 O(3)	–O(1) ⁱⁱⁱ	2.787(7)				2 OW(3) ^v –OW(3) ⁱ	3.381(8)	98.99
average		2.678				average		3.037
		90.00	P(2)			Ca–O Polyhedra		
Al(2)			1 P(2)–O(6)	1.518(5)		Ca(1)		
2 Al(2)	–OH ⁱⁱⁱ	1.892(5)	1	–O(4)	1.534(5)	2 Ca(1)	–O(6)	2.346(5)
2	–O(5)	1.901(5)	1	–O(3)	1.554(5)	2	–OW(2) ^{iv}	2.482(5)
2	–O(2) ⁱⁱ	1.946(5)	1	–O(5)	1.560(5)	2	–OW(2)	2.618(5)
average		1.913	average	1.541		2	–O(2) ⁱⁱ	2.765(5)
2 O(5)	–O(2) ⁱⁱⁱ	2.589(7)				average		2.553
1 OH ⁱⁱⁱ	–OH ⁱⁱⁱ	2.601(7)	1 O(3)–O(4)	2.442(7)	104.52	Ca(2)		
2 O(2)	–O(5)	2.661(7)	1 O(5)–O(6)	2.513(7)	109.45	2 Ca(2)	–OW(1)	2.346(5)
2 O(5)	–OH ⁱⁱ	2.674(7)	1 O(4)–O(5)	2.521(7)	109.13	2	–O(4) ⁱⁱ	2.427(5)
2 O(2)	–OH ⁱ	2.778(7)	1 O(3)–O(6)	2.530(7)	110.88	2	–O(1) ⁱⁱⁱ	2.514(5)
1 O(5)	–OH ⁱ	2.782(7)	1 O(4)–O(6)	2.536(7)	112.39	2	–O(1) ⁱⁱ	2.551(5)
2 O(2)	–O(5) ⁱ	2.844(7)	1 O(3)–O(5)	2.561(7)	110.66	2	–O(3) ⁱ	2.551(5)
average		2.706	average	2.517	109.51	average		2.460
		90.10						

*i = –x, y, 1/2–z; ii = 1/2–x, 1/2–y, –z; iii = 1/2+x, 1/2–y, 1/2+z; iv = x, –y, 1/2+z; v = –x, –y, –z; vi = 1/2–x, 1/2+y, 1/2–z, referred to the coordinates in Table 2 and in Fig. 1.

donors of hydrogen bonds include OW(1), OW(2), OW(3) and OH. We propose the following hydrogen bonds: OW(1)-H ... O(6)ⁱⁱ, 3.03 Å; OW(1)-H ... O(5)ⁱⁱ, 3.18 Å; OW(2)-H ... O(5), 2.60 Å; OW(2)-H ... O(6)^{iv}, 2.93 Å; OW(3)-H ... O(6)ⁱⁱ, 2.70 Å; OW(3)-H ... O(4)^{vi}, 2.80 Å; O-H ... OW(1)ⁱⁱ, 2.93 Å. The angles O-OW-O' compute to O(6)ⁱⁱ-OW(1)-O(5)ⁱⁱ, 84.0°; O(5)-OW(2)-O(6)^{iv}, 131.7°; and O(4)^{vi}-OW(3)-O(6)ⁱⁱ, 113.6°. According to this model, O(4) receives one; O(5) receives two; and O(6) receives three hydrogen bonds.

Although these assignments involve some uncertainty, they receive support from the calculations of electrostatic valence balances shown in Table 5. Here we assign the [PO₄] oxygen a formal charge of -2, OH the charge -1, and H₂O the charge 0 and look for correlations in $\Delta\Sigma$ with the bond distances and the hydrogen bond model. The anions O(4), O(5), and O(6) are all undersaturated by cations other than hydrogens. According to Baur (1970), the O-H ... O' bond-strength is about 1/6 e.s.u. Taking into account the observed distances for O(4), O(5), and O(6), it appears they each receive the H-bonds suggested by O-O' distance arguments. We note that two bonds to O(6) are rather long so that this anion probably exhibits net cation undersaturation, and reveals shorter than average Me-O(6) distances. Finally, we remark that OH donates its bond to OW(1) resulting in shorter than average Al-OH distances.

Although O(2) possesses rather long Al(2)-O(2) and Ca(1)-O(2) distances, it is unlikely that it receives a hydrogen bond owing to its geometrical separation from the donors. It is possible that OW(1) contributes the OW(1)-H ... O(2) 3.09 Å bond instead of OW(1)-H ... O(6)ⁱⁱ, but the resulting O(2)-OW(1)-O(5)ⁱⁱ angle of 50.2° seems unreasonable.

Topological Equivalence of the Octahedral Chains in Montgomeryite and Vauxite

Montgomeryite and vauxite possess the same kind of chains of corner-sharing Al³⁺-O octahedra. The chains and their enveloping [PO₄] tetrahedra are featured in Figure 2. The polyhedral diagram for vauxite was constructed from the atomic coordinates and cell parameters of Baur and Rama Rao (1968).

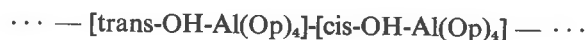
As is typical for many basic ferric and aluminum phosphates, the octahedra are linked by (OH)⁻ ligands. A large number of compounds, the "7 Å chain structures," were listed by Moore (1970). That study stressed the importance of the combinatorial ways in which the enveloping tetrahedral ligands can corner-link to the octahedra, accounting for extensive species diversity among these compounds. In the 7 Å chain structures, *opposing* vertices of each octahedron are involved in links to the neighboring octahedra. We shall define these (OH)⁻ ligands in *trans*-configuration with respect to the octahedral centers. In montgomeryite and vauxite, the octahedra alternately possess (OH)⁻ bridges in

TABLE 5. Montgomeryite. Electrostatic Valence Balances of Cations about Anions

Anion	Coordinating Cation	Σ	$\Delta\Sigma$	Comments
Anions Treated as X ²⁻				
O(1)	P(1)+Al(1)+Ca(2)	2.00	0.00	P(1)-, Al(1)-, Ca(2)-O(1) average.
O(2)	P(1)+Al(2)+Ca(1)	2.00	0.00	P(1)-O(2) average; Al(2)-, Ca(1)-O(2) long.
O(3)	P(2)+Al(1)+Ca(2)	2.00	0.00	P(2)-, Al(1)-, Ca(2)-O(3) average.
O(4)	P(2)+1/2 Mg+Ca(2)	1.67	-.33	P(2)-, Ca(2)-O(4) average; Mg-O(4) short. Receives one H-bond.
O(5)	P(2)+Al(2)	1.75	-.25	Al(2)-O average; P(2)-O(5) long. Receives two H-bonds.
O(6)	P(2)+Ca(1)	1.50	-.50	P(2)-, Ca(1)-O(6) short. Receives three H-bonds.
Anion Treated as X ¹⁻				
OH	Al(1)+Al(2)	1.00	0.00	Al(1)-, Al(2)-OH short. Donates one H-bond.
Anions Treated as X ⁰				
OW(1)	Ca(2)	0.25	+0.25	Ca(2)-OW(1) short. Donates two H-bonds.
OW(2)	2Ca(1)	0.50	+0.50	Ca(1)-OW(2) average. Donates two bonds.
OW(3)	2(1/2 Mg)	0.33	+0.33	Mg-OW(3) long. Donates two bonds.
	sum		0.00	

trans- and *cis*-configurations. In other words, the ligands alternately form opposing octahedral vertices and adjacent vertices. Setting Op = oxygen associated with the [PO₄] tetrahedron, the chain formulae can be written as follows:

montgomeryite



vauxite



For montgomeryite and vauxite, octahedral chains and enveloping tetrahedra lead to compositions [Al₄(OH)₄(PO₄)₆]¹⁰⁻ and [Al₄(OH)₄(H₂O)₄(PO₄)₄]⁴⁻, respectively.

One of the remarkable features of both structures is the striking similarity in the orientations of the octahedra as shown in Figure 2. Such features have also been stressed by Moore (1970) for the 7 Å corner-chain structures, and we offer the empirical statement that the polymerization of the Al³⁺-O (and Fe³⁺-O) octahedra dictates the basic structural features among all these compounds. In montgomeryite and vauxite, the larger cations of lower charge with subsequent weaker bond strengths are intercalated in the remaining spaces in the structures. Thus, Mg, Ca(1), and Ca(2) in the former, and Fe²⁺(1) and Fe²⁺(2) in the latter do not dictate the configurations of these structures (aside from geometrical distortions) as much as do the Al-O octahedral chains.

From these observations we propose that crystal-chemical classification of these and related compounds should proceed from a detailed examination of the polyhedral clusters with greatest bond strength. Such a taxonomy is both natural and efficacious for the silicates and borates and proceeds from the linkage types of tetrahedra in the former and tetrahedra and triangles for the latter. In the basic phosphates, sulfates, arsenates, *etc.*, the polyhedra of greatest bond strength after the tetrahedra must be included as well. A systematic treatment of the basic ferric sulfate structures by Süsse (1970) proceeds from these lines, where the complexes in the structure are the condensed Fe³⁺-OH, O, H₂O-octahedra and their enveloping tetrahedra. The advantages of this classification are manifold: octahedral clusters of interest to the chemist are singled

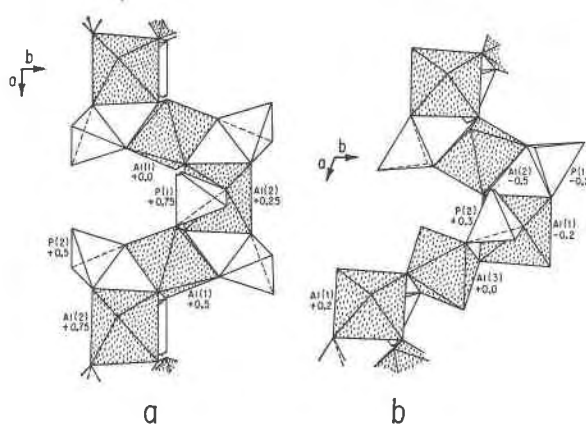


FIG. 2. The Al-O octahedral chains and their enveloping PO₄ tetrahedra in montgomeryite (a) and vauxite (b). The coordinates for vauxite were obtained from Baur and Rama Rao (1968).

out, and it appears that the cluster types may provide information on the mineral's paragenesis. Finally, the multiple roles of water—as ligands bonded to transition metals, at the vertices of polyhedra involving alkalis and alkaline earths, and as zeolitic or channel-filling molecules—are unambiguously distinguished.

Acknowledgments

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