

Stewartite, $\text{Mn}^{2+}\text{Fe}^{3+}_2(\text{OH})_2(\text{H}_2\text{O})_6[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$: Its Atomic Arrangement

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Abstract

Stewartite, $\text{Mn}^{2+}\text{Fe}^{3+}_2(\text{OH})_2(\text{H}_2\text{O})_6[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$ —space group $P\bar{1}$; a 10.398(2) Å, b 10.672(3) Å, c 7.223(3) Å, α 90.10(3)°, β 109.10(2)°, γ 71.83(2)°; $Z = 2$ —is structurally related to the polymorphs, laueite and pseudolaueite. $R(hkl) = 0.072$ for 5034 non-equivalent reflections. Along [102] the structure contains corner-sharing chains of octahedra of composition $[\text{Fe}^{3+}(\text{OH})(\text{H}_2\text{O})(\text{O}_F)_3]$. PO_4 tetrahedra bridge these chains to form sheets of $[\text{Fe}^{3+}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)]^-$ composition oriented parallel to {010}. These sheets are bridged along [010] by *trans*- $\text{Mn}^{2+}(\text{H}_2\text{O})_4(\text{O}_F)_2$ octahedra.

Average distances are Fe(1)-O 2.02 Å, Fe(2)-O 2.01 Å, Fe(3)-O 2.01 Å, Mn-O 2.18 Å, P(1)-O 1.54 Å, and P(2)-O 1.54 Å. The proposed hydrogen-bond model accommodates eighteen distinct bonds.

Introduction

Stewartite, laueite, pseudolaueite, and jahnsite are low temperature, basic, ferric phosphates which occur sporadically in granitic pegmatites where triphylite has suffered retrograde alkali-leaching, oxidation, and hydration. The minute orange-yellow crystals of these species so resemble each other that careful morphological or X-ray study is required for their distinction.

Moore (1970) proposed that these and some other species belong to a family of compounds—the 7 Å octahedral corner-chain structures—whose distinction rests primarily on the isomerisms of (H_2O) and $[\text{PO}_4]$ ligands about these chains. Since stewartite possesses one 7 Å axis, it was natural to assume that its unknown structure may involve a hitherto unreported isomerism. The crystal structures of laueite (Moore, 1965), pseudolaueite (Baur, 1969), and jahnsite (Moore and Araki, 1974) have been determined; and with the present knowledge at hand for the stewartite structure, a detailed analysis of the kinds of isomerism among these structures is desirable.

Stewartite was originally described as a new species by Schaller (1912), although sufficient material was not available for a quantitative wet chemical analysis. Peacor (1963) reported the crystal cell parameters of this triclinic mineral and demonstrated that the complex pseudo-monoclinic cell pro-

posed by Tennyson (1956) could be derived therefrom. On the grounds of a relationship in structure cell parameters, paragenesis, and physical properties to those of laueite, $\text{MnFe}^{3+}_2(\text{OH})_2(\text{H}_2\text{O})_6[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$, Peacor (1963) concluded that stewartite is a polymorph, which is confirmed by our crystal structure analysis.

Experimental

A superior single crystal of stewartite from the Hagendorf pegmatite, Bavaria, measured 0.36 mm along a^* , 0.19 mm along b^* , and 0.12 mm along c^* . The crystal was mounted with the a -axis parallel to the φ -axis on a PICKER automated diffractometer. Other salient details include: graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.7093$ Å); maximum $\sin \theta/\lambda = 0.75$; twenty-second background counting times; scan rate 1.0°/minute; half-angle scan 1.8°. Five-thousand thirty-four reflections were corrected for absorption by the Gaussian integral method described by Burnham (1966) utilizing six points. For $I(hkl) < 2\sigma(I(hkl))$, the reflections were set as $\sigma(I(hkl))$.

Solution and Refinement of the Structure

Least-squares refinement of twelve monitor reflections provided the cell parameters a 10.398(2) Å, b 10.672(3) Å, c 7.223(3) Å, α 90.10(3)°, β 109.10(2)°, γ 71.83(2)°. A Wilson plot presented

a nearly perfect fit with the centrosymmetric model, and we elected space group $P\bar{1}$. Three-dimensional Patterson synthesis established a model including four non-equivalent transition metal atoms and two non-equivalent phosphorus atoms. These provided enough scattering matter for locating all remaining non-hydrogen atoms through Fourier electron density synthesis.

Three-dimensional full-matrix refinement using a local modification of the familiar ORFLS least-squares program of Busing, Martin, and Levy (1962) led to convergence for the atomic coordinates and isotropic thermal vibration parameters of all twenty-four independent non-hydrogen atoms. We included correction for secondary extinction and anomalous dispersion of the Fe, Mn, and P atoms. The scattering curves for Fe^{3+} , Mn^{2+} , P^{5+} and O^{2-} derive from Cromer and Mann (1968). For all 5034 reflections, $R(hkl): \sum ||F(\text{obs})| - |F(\text{calc})|| / \sum |F(\text{obs})| = 0.072$. Atomic coordinate parameters appear in Table 1, and the structure factors in Table 2.¹

Discussion of the Structure

The stereochemical relationships among stewartite and the other related structures shall be discussed in another paper; we report here the general features of the stewartite geometry.

In stewartite (Fig. 1) three non-equivalent Fe^{3+} -O octahedra—Fe(1), Fe(2), and Fe(3)—are linked at opposing vertices by hydroxyl groups OH(1) and OH(2) to form corner-sharing chains of octahedra like those in laueite, pseudolaueite, and metavauxite. These chains run parallel to the [102] direction, an unanticipated feature since typical chain repeats are between 6.9 and 7.5 Å and it was earlier believed that the chain direction would be [001]. However, $[102]/2 = 7.39$ Å, which compares with the chain repeat $b = 7.43$ Å in pseudolaueite, $c = 7.14$ Å in laueite, and $b = 7.14$ Å in jahnsite.

In common with the structures of laueite and pseudolaueite, three of the four oxygens in the PO_4 tetrahedra bridge the octahedral chains to form a dense sheet of composition $[\text{Fe}^{3+}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)]^{2-}$ like that found by Baur (1969) in laueite and pseudo-

TABLE 1. Stewartite: Atomic Coordinate and Isotropic Thermal Vibration Parameters*

Atom	x	y	z	B (Å ²)
Mn	0.27273 (6)	0.48931 (5)	0.64620 (8)	1.22 (1)
Fe(1)	0.0000	0.0000	0.0000	0.73 (1)
Fe(2)	0.5000	0.0000	0.0000	0.78 (1)
Fe(3)	.24996 (4)	.99745 (4)	.50902 (6)	0.62 (1)
P(1)	.90510 (8)	.18642 (7)	.3397 (1)	0.60 (1)
O(1)	.0588 (3)	.1258 (2)	.4888 (3)	.92 (3)
O(2)	.8870 (3)	.1210 (2)	.1445 (3)	.96 (3)
O(3)	.8698 (3)	.3356 (2)	.2941 (3)	1.05 (3)
O(4)	.8002 (3)	.1617 (2)	.4336 (3)	.91 (3)
P(2)	.45901 (8)	.17736 (7)	.5960 (1)	.60 (1)
O(5)	.3118 (3)	.1579 (2)	.4947 (3)	.80 (3)
O(6)	.4372 (3)	.3260 (2)	.6072 (3)	1.14 (3)
O(7)	.5545 (3)	.1265 (2)	.4695 (3)	.82 (3)
O(8)	.5366 (3)	.1008 (2)	.8042 (3)	1.04 (3)
OH(1)	.1798 (3)	.9910 (2)	.2156 (3)	1.01 (3)
OH(2)	.3179 (3)	.0006 (2)	.8040 (3)	.99 (3)
OW(1)	.0176 (3)	.1606 (3)	.8587 (4)	1.41 (4)
OW(2)	.3893 (3)	.1750 (3)	.0894 (4)	1.66 (4)
OW(3)	.1427 (3)	.3641 (3)	.6592 (5)	2.12 (5)
OW(4)	.1516 (3)	.5428 (3)	.3282 (4)	1.81 (4)
OW(5)	.4115 (3)	.6099 (3)	.6346 (4)	1.60 (4)
OW(6)	.3732 (4)	.4408 (3)	.9668 (5)	2.22 (5)
OW(7)	.0969 (3)	.3258 (3)	.1534 (5)	2.09 (5)
OW(8)	.2954 (3)	.6554 (3)	.1527 (4)	1.97 (5)

* Estimated standard errors refer to the last digit.

laueite. In stewartite, these sheets are oriented parallel to {010}. Accordingly, stewartite exhibits perfect {010} cleavage. Designating as O_P the oxygen associated with the PO_4 tetrahedron, Fe(1) and Fe(2) are surrounded by $2(\text{O}_P) + 2(\text{H}_2\text{O}) + 2(\text{OH})$, and Fe(3) by $4(\text{O}_P) + 2(\text{OH})$. Thus, the octahedral chain fraction can be written $[\text{Fe}^{3+}(\text{OH})(\text{H}_2\text{O})(\text{O}_P)_3]$.

The *trans*- $\text{Mn}^{2+}(\text{H}_2\text{O})_4(\text{O}_P)_2$ octahedron acts as a bridge between sheets along the [010] direction in the same manner as the $\text{Mn}^{2+}(\text{H}_2\text{O})_4(\text{O}_P)_2$ octahedra in the laueite and pseudolaueite structures. Two non-equivalent water molecules, Ow(7) and Ow(8), which occur in the structure, do not coordinate directly to metals but donate and receive hydrogen bonds. Thus, as in laueite and pseudolaueite, the stewartite composition is $\text{Mn}^{2+}\text{Fe}^{3+}_2(\text{OH})_2(\text{H}_2\text{O})_6[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$.

Bond Distances and Angles

Table 3 provides the bond distances and angles for the Fe^{3+} -O Mn^{2+} -O octahedra, and the PO_4 tetrahedra. The range of angles for Fe^{3+} and Mn^{2+} from 85° to 95° indicates that the octahedra are only mildly distorted. The tetrahedral angles range from 108° to 112° . The average metal-oxide distances

¹ To obtain a copy of Table 2, order NAPS Document 02459 (52 pages) by remitting \$1.50 for microfiche or \$5.00 for photocopies up to 30 pages, 15¢ each additional page, payable to Microfiche Publications, 305 East 46th Street, New York, N.Y. 10017. Please check the most recent issue of this journal for the current address and prices.

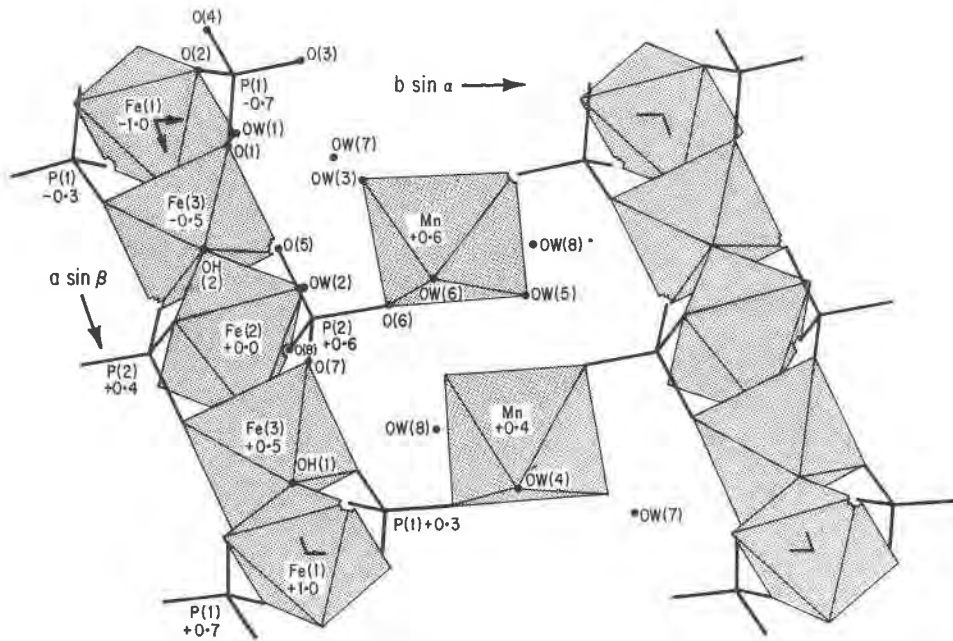


FIG. 1. The Stewartite crystal structure viewed down [001]. The Fe³⁺-O and Mn²⁺-O octahedra are stippled and the P-O bonds are drawn as spokes. Heights of the Fe³⁺-O octahedra are given in fractional coordinates corresponding to a chain. The octahedral vertices are broken if the equivalent tetrahedron above or below links to it.

all fall within their expected range. Judged by the reasonably low isotropic thermal vibration parameters for Mn²⁺ and Fe³⁺ (0.6 to 1.2 Å²) and the average distances for Fe³⁺-O (between 2.01 and

2.02 Å) and Mn-O (2.18 Å), the Stewartite chemical composition exhibits little substitution by other cations and thus the crystal we studied is a fairly pure end-member compound. Despite the lack of a

TABLE 3. Stewartite: Interatomic Distances and Angles*

Fe(1)		Fe(2)		Fe(3)		Mn	
Fe(1)-OH(1)	1.977Å	2 Fe(2)-OH(2)	1.955	Fe(3) - O(1) _i	1.989	Mn - O(6)	2.119
- O(2)	1.997	2 - O(8)	1.979	- O(7) _i	2.005	- O(3)	2.136
-OW(1)	2.082	2 -OW(2)	2.090	- O(4) _i	2.006	-OW(6)	2.192
average	2.019	average	2.008	-OH(1)	2.011	-OW(3)	2.197
				-OH(2)	2.017	-OW(4)	2.202
				- O(5)	2.022	-OW(5)	2.231
				average	2.008	average	2.180
OH(1) - O(2) ¹	2.791 90.8°	2 OH(2) - O(8) ²	2.767 89.4	OH(2) - O(4) ¹	2.718 85.0	O(3) -OW(6)	2.961 86.3
OH(1) - O(2)	2.829 89.2	2 OH(2) - O(8) _i	2.797 90.6	O(1) - O(5)	2.742 86.2	O(6) -OW(5)	2.970 86.0
OH(1) -OW(1)	2.834 88.5	2 O(8) -OW(2) _i	2.838 88.4	OH(2) _i - O(5)	2.770 86.6	O(3) -OW(5)	3.012 87.2
O(2) -OW(1) _i	2.859 91.0	2 OH(2) -OW(2) _i	2.848 89.4	O(4) _i - O(7) _i	2.785 88.0	O(6) -OW(6)	3.013 86.7
OH(1) -OW(1) _i	2.908 91.5	2 OH(2) -OW(2) _i	2.876 90.6	OH(2) - O(1)	2.824 89.6	O(6) -OW(4)	3.050 94.3
O(2) -OW(1) _i	2.911 89.0	2 O(8) -OW(2)	2.918 91.6	OH(1) - O(1) _i	2.833 90.2	O(3) -OW(4)	3.063 89.8
average	2.855 90.0	average	2.841 90.0	OH(2) - O(7) _i	2.843 89.9	OW(3) -OW(4)	3.103 89.7
				O(5) - O(7) _i	2.847 90.3	O(6) -OW(3)	3.105 92.0
				O(1) - O(4) _i	2.822 94.0	OW(4) -OW(5)	3.161 90.9
				OH(1) - O(4) _i	2.929 93.6	O(3) -OW(3)	3.189 94.7
				OH(1) - O(5)	2.969 94.8	OW(5) -OW(6)	3.203 92.8
				average	2.839 90.0	average	3.073 90.0
P(1)		P(2)		Hydrogen Bonds			
P(1) - O(3)	1.528	P(2) - O(6)	1.536	OW(1) - O(1)	2.85	OW(6) -OW(5)	2.93
- O(1)	1.536	- O(7)	1.539	OW(1) -OW(7)	2.84	OW(6) -OW(8)	2.69
- O(4)	1.543	- O(8)	1.542	OW(2) - O(7)	2.67	OW(7) - O(5)	2.86
- O(2)	1.554	- O(5)	1.543	OW(2) -OW(6)	2.91	OW(7) - O(3)	2.83
average	1.540	average	1.540	OW(3) - O(5)	2.88	OW(8) - O(2)	2.90
				OW(3) -OW(4)	2.94	OW(8) - O(6)	2.82
O(1) - O(4)	2.486 107.7	O(6) - O(7)	2.485 107.8	OW(4) -OW(7)	2.76	OH(1) - O(8)	2.77
O(2) - O(3)	2.511 109.1	O(5) - O(7)	2.504 108.7	OW(4) -OW(8)	2.76	OH(2) - O(2)	2.93
O(1) - O(3)	2.511 110.0	O(7) - O(8)	2.506 108.8	OW(5) - O(4)	2.64		
O(3) - O(4)	2.511 109.7	O(5) - O(6)	2.516 109.6	OW(5) - O(8)	2.64		
O(2) - O(4)	2.519 108.9	O(6) - O(8)	2.523 110.1	OW(5) - O(6)	2.91		
O(1) - O(2)	2.554 111.4	O(5) - O(8)	2.554 111.7				
average	2.515 109.5	average	2.515 109.5				

* i = -x, -y, -z applied to coordinates in Table 1. Errors are ± 0.003Å in Mn-O distances and ± 0.004Å in O-O' distances.

complete wet chemical analysis on the Hagendorf material, there is little reason to doubt the formula proposed in this study. Although Baur (1969) discusses the possible role of Mn^{3+} in stabilizing the laeute structure, the very existence of the paravauxite ($Fe^{2+}Al_2$) and gordonite ($MgAl_2$) isotypes argues well that stewartite, laeute, and pseudolaueite are indeed polymorphs.

Hydrogen Bonds

We have attempted to locate all the possible hydrogen bonds in the stewartite structure from geometrical considerations and accepted only those distances between 2.6 and 3.1 Å. A sensible model is summarized in Table 3 and in Figure 2.

In general, the model closely corresponds to those proposed by Baur (1969) for laeute and pseudolaueite. We find it appropriate to utilize his system of tabulating hydrogen donors and acceptors toward a complete list of the electrostatic bond strengths. In this model, the O-H donor is given a value of +5/6 and the H...O acceptor a value of +1/6. Table 4 lists the electrostatic bond strengths and their sums for all the oxygen atoms. We note that significantly undersaturated oxygens—O(3), OH(1), and OH(2)—possess shorter-than-average polyhedral distances and that significantly oversaturated oxygens—Ow(1), Ow(2), Ow(4), Ow(5), and Ow(6)—possess longer-than-average distances. The Ow(7) and Ow(8) water molecules, which do not participate as ligands, are exactly neutral since they receive as well as donate two bonds each.

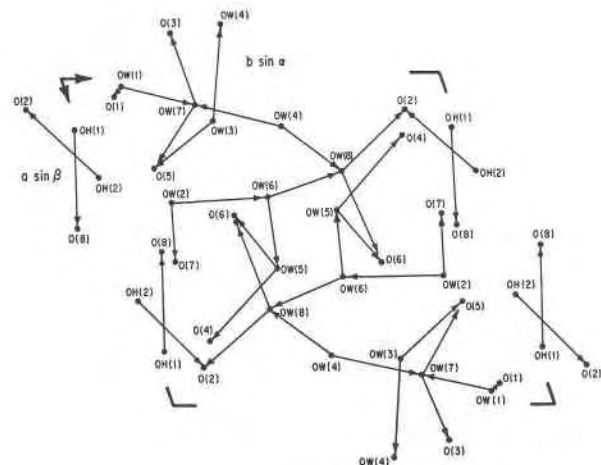


FIG. 2. Hydrogen bonding scheme in stewartite referring to the structure diagram in Figure 1. Heads of arrows point to the hydrogen bond acceptors. The donor bonds are drawn only if they originate in the unit cell.

TABLE 4. Stewartite: Electrostatic Bond Strengths and Their Sums about the Anions*

Anion	Mn ²⁺	Fe ³⁺	P ⁵⁺	H(d)	H(a)	Σ	Me-O		
							Mn	Fe	P
O(1)		3/6	5/4		1/6	1.92	-	0	
O(2)		3/6	5/4		1/6+1/6	2.08	-	+	
O(3)	2/6		5/4		1/6	1.75	-	-	
O(4)		3/6	5/4		1/6	1.92	0	0	
O(5)		3/6	5/4		1/6+1/6	2.08		+	0
O(6)	2/6		5/4		1/6+1/6	1.92	-	+	0
O(7)		3/6	5/4		1/6	1.92	0	0	
O(8)		3/6	5/4		1/6	1.92	-	0	
OH(1)		3/6+3/6		5/6		1.83	-	0	
OH(2)		3/6+3/6		5/6		1.83	-	0	
Ow(1)		3/6		5/6+5/6		2.17	+	+	
Ow(2)		3/6		5/6+5/6		2.17	+	+	
Ow(3)		3/6		5/6+5/6		2.17	+	+	
Ow(4)	2/6			5/6+5/6	1/6	2.17	+	+	
Ow(5)	2/6			5/6+5/6	1/6	2.17	+	+	
Ow(6)	2/6			5/6+5/6	1/6	2.17	+	+	
Ow(7)				5/6+5/6	1/6+1/6	2.00			
Ow(8)				5/6+5/6	1/6+1/6	2.00			

*Me-O refers to distances which are greater than (+), less than (-), or within (0) 2σ of the interatomic error referred to the polyhedral average. H(d) = hydrogen donor, H(a) = hydrogen bond acceptor.

One intriguing question arises regarding the relative stability of the various stereoisomers and the necessity for a compatible hydrogen-bonding scheme. We feel that the hydrogen bonds do not dictate which of the octahedral chain stereoisomers are stable since their forces are relatively weak and since their range of bond angles (61° to 144° in stewartite) allows considerable geometrical freedom. In addition, the corner-sharing polyhedra can twist significantly to accommodate these bonds. Finally, non-ligand water molecules may fit into the structure to increase the likelihood of a network of satisfied hydrogen bonds.

We note that hydrogen bonds such as OH(1)...O(8) and OH(2)...O(2) are similarly oriented as in the laeute and pseudolaueite OH(5)...O(p2) since the immediate neighborhoods in these structures are all similar. The highly aquated *trans*-Mn(H₂O)₄(O_P)₂ octahedron, however, has a different neighborhood in all these structures as a result of the discrete differences in stereoisomerism within the sheets of Fe³⁺-O octahedra and P-O tetrahedra.

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