American Mineralogist, Volume 59, pages 1272–1276, 1974

Stewartite, $Mn^{2+}Fe^{3+}_2(OH)_2(H_2O)_6[PO_4]_2 \cdot 2H_2O$: Its Atomic Arrangement

PAUL BRIAN MOORE, AND TAKAHARU ARAKI

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

Abstract

Stewartite, $Mn^{2+}Fe^{3+}_2(OH)_2(H_2O)_6[PO_4]_2 \cdot 2H_2O$—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 $[Fe^{3+}(OH)(H_2O)(O_P)_3]$. PO_4 tetrahedra bridge these chains to form sheets of $[Fe^{3+}(OH)(H_2O)(PO_4)]^{1-}$ composition oriented parallel to {010}. These sheets are bridged along [010] by *trans*-$Mn^{2+}(H_2O)_4(O_P)_2$ 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 [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 proposed 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, $MnFe^{3+}_2(OH)_2(H_2O)_6[PO_4]_2 \cdot 2H_2O$, 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 Mo$K\alpha$ 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^{0+} and O^{1-} derive from Cromer and Mann (1968). For all 5034 reflections, $R(hkl)$: $\Sigma||F(\text{obs})|-|F(\text{calc})||/\Sigma|F(\text{obs})| = 0.072$. 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 $[Fe^{3+}(OH)(H_2O)(PO_4)]^{1-}$ like that found by Baur (1969) in laueite and pseudolaueite. 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 $2(O_P) + 2(H_2O) + 2(OH)$, and Fe(3) by $4(O_P) + 2(OH)$. Thus, the octahedral chain fraction can be written $[Fe^{3+}(OH)(H_2O)(O_P)_3]$.

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.

The *trans*-$Mn^{2+}(H_2O)_4(O_P)_2$ octahedron acts as a bridge between sheets along the [010] direction in the same manner as the $Mn^{2+}(H_2O)_4(O_P)_2$ 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 $Mn^{2+}Fe^{3+}_2(OH)_2(H_2O)_6[PO_4]_2 \cdot 2H_2O$.

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.

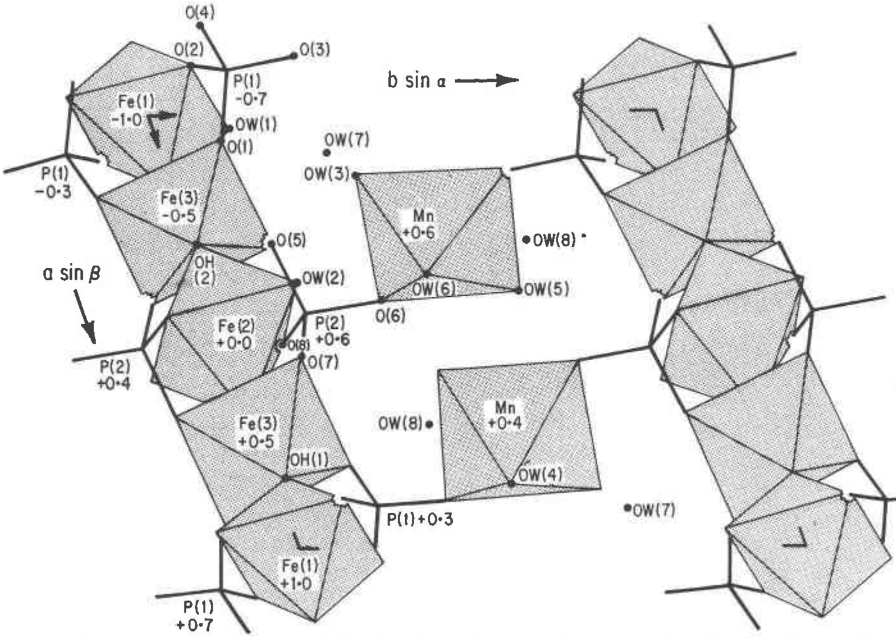

FIG. 1. The stewartite crystal structure viewed down [001]. The Fe^{3+}-O and Mn^{2+}-O octahedra are stippled and the P-O bonds are drawn as spokes. Heights of the Fe^{3+}-O octahedra are given in fractional coordinates corresponding to a chain. The octahedral vertices are broken if the equivalent tetrahedron above or below links to it.

all fall within their expected range. Judged by the reasonably low isotropic thermal vibration parameters for Mn^{2+} and Fe^{3+} (0.6 to 1.2 Å^2) and the average distances for Fe^{3+}-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)			
2	Fe(1)-OH(1)	1.977Å	
2	- O(2)	1.997	
2	-OW(1)	2.082	
	average	2.019	
2	OH(1)- O(2)^i	2.791	90.8°
2	OH(1)- O(2)	2.829	89.2
2	OH(1)-OW(1)	2.834	88.5
2	O(2)-OW(1)	2.859	91.0
2	OH(1)-OW(1)^i	2.908	91.5
2	O(2)-OW(1)^i	2.911	89.0
	average	2.855	90.0

Fe(2)			
2	Fe(2)-OH(2)	1.955	
2	- O(8)	1.979	
2	-OW(2)	2.090	
	average	2.008	
2	OH(2)- O(8)^i	2.767	89.4
2	OH(2)- O(8)	2.797	90.6
2	O(8)-OW(2)^i	2.838	88.4
2	OH(2)-OW(2)	2.848	89.4
2	OH(2)-OW(2)^i	2.876	90.6
2	O(8)-OW(2)	2.918	91.6
	average	2.841	90.0

Fe(3)		
Fe(3) - O(1)	1.989	
- O(7)^i	2.005	
- O(4)^i	2.006	
-OH(1)	2.011	
-OH(2)	2.017	
- O(5)	2.022	
average	2.008	
OH(2) - O(4)^i	2.718	85.0
O(1) - O(5)	2.742	86.2
OH(2) - O(5)	2.770	86.6
O(4)^i - O(7)^i	2.785	88.0
OH(2) - O(1)	2.824	89.6
OH(1) - O(1)	2.833	90.2
OH(2) - O(7)^i	2.843	89.9
OH(1) - O(7)^i	2.847	90.3
O(5) - O(7)^i	2.889	91.7
O(1) - O(4)^i	2.922	94.0
OH(1) - O(4)^i	2.929	93.6
OH(1) - O(5)	2.969	94.8
average	2.839	90.0

Mn		
Mn - O(6)	2.119	
- O(3)	2.136	
-OW(6)	2.192	
-OW(3)	2.197	
-OW(4)	2.202	
-OW(5)	2.231	
average	2.180	
O(3)-OW(6)	2.961	86.3
O(6)-OW(5)	2.970	86.0
O(3)-OW(5)	3.012	87.2
OW(3)-OW(6)	3.013	86.7
O(6)-OW(6)	3.049	90.0
O(6)-OW(4)	3.050	94.3
O(3)-OW(4)	3.063	89.8
OW(3)-OW(4)	3.103	89.7
O(6)-OW(3)	3.105	92.0
OW(4)-OW(5)	3.161	90.9
O(3)-OW(3)	3.189	94.7
OW(5)-OW(6)	3.203	92.8
average	3.073	90.0

P(1)		
P(1) - O(3)	1.528	
- O(1)	1.536	
- O(4)	1.543	
- O(2)	1.554	
average	1.540	
O(1) - O(4)	2.486	107.7
O(2) - O(3)	2.511	109.1
O(1) - O(3)	2.511	110.0
O(3) - O(4)	2.511	109.7
O(2) - O(4)	2.519	108.9
O(1) - O(2)	2.554	111.4
average	2.515	109.5

P(2)		
P(2) - O(6)	1.536	
- O(7)	1.539	
- O(8)	1.542	
- O(5)	1.543	
average	1.540	
O(6) - O(7)	2.485	107.8
O(5) - O(7)	2.504	108.7
O(7) - O(8)	2.506	108.8
O(5) - O(6)	2.516	109.6
O(6) - O(8)	2.523	110.1
O(5) - O(8)	2.554	111.7
average	2.515	109.5

Hydrogen Bonds			
OW(1)- O(1)	2.85	OW(6)-OW(5)	2.93
OW(1)-OW(7)	2.84	OW(6)-OW(8)	2.69
OW(2)- O(7)	2.67	OW(7)- O(5)	2.86
OW(2)-OW(6)	2.91	OW(7)- O(3)	2.83
OW(3)- O(5)	2.88	OW(8)- O(2)	2.90
OW(3)-OW(4)	2.94	OW(8)- O(6)	2.82
OW(4)-OW(7)	2.76	OH(1)- O(8)	2.77
OW(4)-OW(8)	2.76	OH(2)- O(2)	2.93
OW(5)- O(4)	2.64		
OW(5)- O(6)	2.91		

*i= -x,-y-z applied to coordinates in Table 1. Errors are ± 0.003Å in Me-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 laueite structure, the very existence of the paravauxite ($Fe^{2+}Al_2$) and gordonite ($MgAl_2$) isotypes argues well that stewartite, laueite, 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 laueite 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.

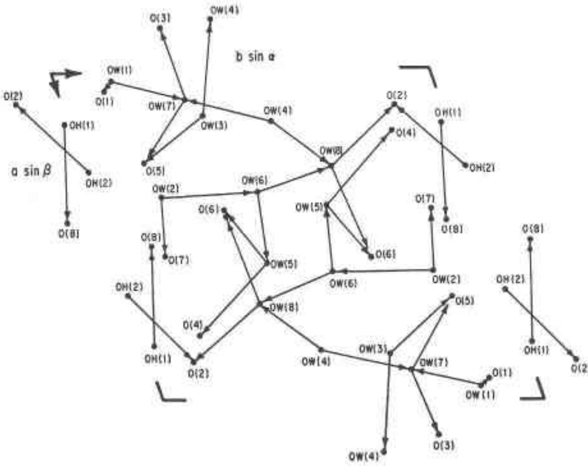

FIG. 2. Hydrogen bonding scheme in stewartite referring to the structure diagram in Figure 1. Heads of arrows point to the hydrogen bond acceptors. The donor bonds are drawn only if they originate in the unit cell.

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

							Me-O		
Anion	Mn^{2+}	Fe^{3+}	P^{5+}	H(d)	H(a)	Σ	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)	2/6			5/6+5/6		2.00	+		
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 laueite and pseudolaueite OH(5) . . . O(p2) since the immediate neighborhoods in these structures are all similar. The highly aquated *trans*-$Mn(H_2O)_4(O_P)_2$ octahedron, however, has a different neighborhood in all these structures as a result of the discrete differences in stereoisomerism within the sheets of Fe^{3+}-O octahedra and P-O tetrahedra.

Acknowledgments

Fine crystals of Hagendorf stewartite were personally collected by Dr. Gerhard Jung of Albbruck, Hochrhein.

This study was supported by the National Science Foundation Grant GA 40543 and the Sloan Foundation Grant-in-Aid BR-1489 awarded to P.B.M.

References

BAUR, W. H. (1969) A comparison of the crystal structures of pseudolaueite and laueite. *Am. Mineral.* **54,** 1312–1323.

BURNHAM, C. W. (1966) Computation of absorption corrections, and the significance of the end effect. *Am. Mineral.* **51,** 159–167.

BUSING, W. A., K. O. MARTIN, AND H. A. LEVY (1962) ORFLS, a Fortran crystallographic least-squares program. *U.S. Oak Ridge Nat. Lab.* ORNL-TM-**305.**

CROMER, D. T., AND J. B. MANN (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.* **A24,** 321–324.

MOORE, P. B. (1965) The crystal structure of laueite, $Mn^{2+}Fe^{3+}_2(OH)_2(PO_4)_2(H_2O)_6 \cdot 2H_2O$. *Am. Mineral.* **50,** 1884–1892.

——— (1970) Structural hierarchies among minerals containing octahedrally coordinating oxygen: I. Stereoisomerism among corner-sharing octahedral and tetrahedral chains. *Neues Jahrb. Mineral. Monatsh.* **1970,** 163–173.

———, AND T. ARAKI (1974) Jahnsite, $CaMn^{2+}Mg_2(H_2O)_8Fe^{3+}_2(OH)_2[PO_4]_4$: A novel stereoisomerism of ligands about octahedral corner-chains. *Am. Mineral.* **59,** 964–973.

PEACOR, D. R. (1963) Unit cell and space group of stewartite. *Am. Mineral.* **48,** 913–914.

SCHALLER, W. T. (1912) New manganese phosphates from the gem tourmaline field of Southern California. *J. Wash. Acad. Sci.* **2,** 143–145.

TENNYSON, CH. (1956) Das Stewartit Problem. *Naturwissenshaften,* **43,** 128–129.

Manuscript received, May 13, 1974; accepted for publication, July 9, 1974.