

THE CRYSTAL STRUCTURE OF LAUEITE,
 $\text{Mn}^{2+}\text{Fe}_2^{3+}(\text{OH})_2(\text{PO}_4)_2(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$

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ABSTRACT

Laueite, $\text{Mn}^{2+}\text{Fe}_2^{3+}(\text{OH})_2(\text{PO}_4)_2(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$, triclinic $P \bar{1}$, $a = 5.28$, $b = 10.66$, $c = 7.14$ Å, $\alpha = 107^\circ 55'$, $\beta = 110^\circ 59'$, $\gamma = 71^\circ 07'$, $Z = 1$, has two known isotypes and three polymorphs. Its crystal structure consists of infinite chains of vertex-linked oxygen octahedra, isolated oxygen octahedra, and tetrahedral tetradentate PO_4^{-3} groups. There are two different kinds of structural water in laueite: ligand water and "zeolitic" water.

Stereoisomeric considerations lead to other structures based on the same motifs as in laueite but with different symmetries and cell dimensions. Two such structures may be represented in the polymorphs strunzite and stewartite.

INTRODUCTION

Laueite, $\text{Mn}^{2+}\text{Fe}_2^{3+}(\text{OH})_2(\text{PO}_4)_2(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$, is one of the more widespread of the hydrothermally reworked products of triphylite, though never occurring in any significant amount at any single locality. Two isotypes of laueite exist—paravauxite, $\text{Fe}^{2+}\text{Al}_2(\text{OH})_2(\text{PO}_4)_2(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$, and gordonite, $\text{MgAl}_2(\text{OH})_2(\text{PO}_4)_2(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$. Three polymorphs of laueite are known—strunzite, stewartite and pseudolaueite.

Laueite and its polymorphs belong to a sizable group of compounds referred to as Fe-Mn orthophosphate hydrates. At least 58 compounds have been recorded and the crystal structures are known for eight of them—strengite, $\text{Fe}(\text{PO}_4)(\text{H}_2\text{O})_2$; vivianite, $\text{Fe}_3(\text{PO}_4)_2(\text{H}_2\text{O})_8$; ludlamite, $\text{Fe}_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$; eosphorite,² $\text{MnAl}(\text{PO}_4)(\text{OH})_2(\text{H}_2\text{O})$; scorzalite and lipscombite,¹ $\text{FeAl}_2(\text{OH})_2(\text{PO}_4)_2$; heterosite, $\text{Fe}^{3+}(\text{PO}_4) \cdot x\text{H}_2\text{O}$; and phosphoferrite, $\text{Fe}_3(\text{PO}_4)_2(\text{H}_2\text{O})_3$. If the closely related (but as yet essentially unstudied) Fe-Mn orthoarsenate hydrates are included, at least another 22 compounds can be added to the list.

The Fe-Mn orthophosphate and orthoarsenate hydrates belong to a large class of compounds known as coordination complexes. With the advent of ligand field and crystal field theory, such compounds have become of considerable experimental and theoretical interest.

The laueite structure was undertaken in order to augment with more experimental evidence, a general classification scheme for Fe-Mn orthophosphate hydrates, which is the subject of an ensuing paper. It was further hoped that the structures of some of the laueite polymorphs could be inferred. The results are encouraging.

¹ This paper constitutes a part of a PhD thesis submitted to the Department of Geophysical Sciences, University of Chicago.

² Aluminum is octahedrally coordinated.

EXPERIMENTAL WORK

A clear reddish-orange wedge-shaped $0.16 \times 0.32 \times 0.50$ mm crystal, associated with its polymorphs strunzite, stewartite, and pseudolaueite, all implanted upon siderite and ludlamite from the Palermo No. 1 Quarry, North Groton, New Hampshire, was used in this study.

The cell data of laueite given by Strunz (1954) were confirmed. His data were used in this study and are listed in Table 1 along with the data for the polymorphs. An intensity scale of 32 units was prepared from the

TABLE 1. CELL DATA OF LAUEITE AND ITS POLYMORPHS

	Laueite	Stewartite	Strunzite	Pseudolaueite
<i>a</i>	5.28	2×5.23	9.80	9.57
<i>b</i>	10.66	10.77	18.06	7.45
<i>c</i>	7.14 Å	7.25	7.34	10.16
α	$107^{\circ}55'$	$90^{\circ}35'$	$90^{\circ}0'$	$90^{\circ}0'$
β	$110^{\circ}59'$	$109^{\circ}58'$	$100^{\circ}10'$	$104^{\circ}40'$
γ	$71^{\circ}07'$	$71^{\circ}21'$	$90^{\circ}0'$	$90^{\circ}0'$
Z	1	2×1	4	2
S.G.	$P\bar{1}$	$P1$	$C2/c$	mono. ?
Ref.	Strunz (1954)	Peacor (1963)	Fron del (1957)	Strunz (1956)

crystal selected for study and 637 independent intensities were visually estimated from *hk0*, *hk1*, *hk2*, and *0kl* levels using Weissenberg equi-inclination camera and Zr-filtered Mo $K\alpha$ radiation. Four photographs were prepared for each of the levels, using 48-, 24-, 12-, and 6-hour exposures. Absorption corrections were made using the program GNABS of Burnham (1963). Scattering curves were prepared for Fe^{3+} , Mn^{2+} , P^0 , and O^{-1} , calculated from self-consistent wave functions and listed in International Tables, V. 3 (1962). All computations were done on the IBM 7090 computer at the University of Chicago Institute for Computer Research.

STRUCTURE DETERMINATION

The Patterson projections $P(xy)$ and $P(yz)$ showed Fe, Mn residing in special positions at $0,0,0$; $0, \frac{1}{2}, 0$; and $0, \frac{1}{2}, \frac{1}{2}$ for the origin chosen. Assuming a centrosymmetric structure, there remains to be found one phosphorus and nine oxygen atoms, all in general positions. The $P(xy)$ map (Fig. 1) immediately revealed the prominent vector $2Fe_{01} - P_{xy}$ and *xy* coordinates of the phosphorus atom were derived. This vector is labelled "A."

Since the metals reside in special positions and since there is still an insufficiency of located scattering matter for meaningful sign determina-

tions, it was decided to locate some of the oxygens from consideration of cell geometry.

The structure is assumed to be composed of linkages of tetrahedra and octahedra, the ligands being the tetradentate PO_4^{3-} group, OH^- ions, and H_2O molecules. The specification of the total amount of "ligand-water" in the cell is of critical importance. At first glance, the laueite stoichiometry suggests isolated octahedra (*i.e.* not bonded to other octahedra) since $\Sigma\text{O}:\Sigma\text{Fe}$, $\text{Mn}=6:1$. This, of course, assumes that all water is octahedrally bonded. Since the distance $\text{Fe}_{0\frac{1}{2}}-\text{Fe}_{0\frac{1}{2}}$ is 3.57

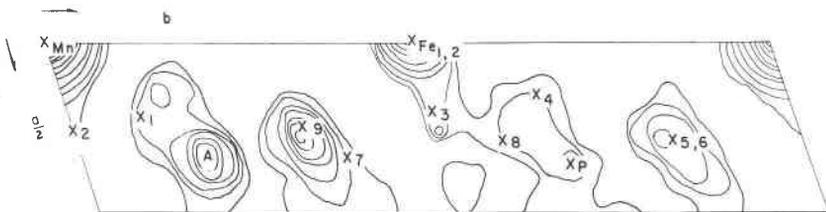


FIG. 1. $P(xy)$ of laueite. Final coordinates of atoms are superposed.

\AA , a structure composed exclusively of isolated octahedra was ruled out for steric reasons. However, this interatomic distance suggests a vertex-linked chain of octahedra, assuming $\text{Fe}^{3+}-\text{O}=1.95 \text{\AA}$.

Due to a metal at the origin, $P(xy)$ should have superimposed a map of the "molecule." This is indeed true, and 8 oxygen positions were located with help from a packing model of vertex-linked octahedral chains and connecting PO_4^{3-} tetrahedra and a Fourier projection was prepared. A 3-cycle least squares refinement, using the ORFLS program of Busing *et al.* (1962) resulted in

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = .27.$$

The remaining oxygen, belonging to a non-octahedrally bonded water, was located and 3 more cycles using all Fe, Mn, P and O positions resulted in $R_{hk0}=.11$. The final atom positions, superposed on the Patterson map (Fig. 1), are marked by "X."

The constraints of coordinates on the octahedrally coordinated oxygens combined with $P(yz)$ resulted in determination of the yz -coordinates after three Fourier projections, with final $R_{0kl}=.15$. A 2-cycle three dimensional refinement with fixed temperature factors (B set to 1.0) gave $R=.14$. The temperature factors were then released and after two more cycles, $R=.122$.

Coordinates and isotropic temperature factors are presented in Table 2. Interatomic distances are given in Table 3. Observed and calculated structure factors are available upon request. None of the intensities gathered were omitted from the final refinement.

TABLE 2. COORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF LAUEITE

Atom	x	y	z	B
Mn	0	0	0	1.75 ± .08
Fe ₁	0	$\frac{1}{2}$	0	0.71 ± .08
Fe ³	0	$\frac{1}{2}$	$\frac{1}{2}$	0.68 ± .07
P	.3460 ± .0012	.6700 ± .0006	.9279 ± .0014	0.78 ± .08
O ₁	.2281 ± .0032	.1121 ± .0014	.9620 ± .0033	1.98 ± .28
O ₂	.2426 ± .0031	.0046 ± .0015	.3218 ± .0034	3.00 ± .33
O ₃	.1552 ± .0032	.5009 ± .0015	.2952 ± .0032	1.30 ± .25
O ₄ ¹	.1666 ± .0032	.6539 ± .0015	.0410 ± .0038	0.90 ± .24
O ₅ ²	.2618 ± .0031	.8016 ± .0015	.5076 ± .0033	2.55 ± .32
O ₆ ¹	.2717 ± .0032	.8188 ± .0015	.9057 ± .0033	1.34 ± .25
O ₇ ¹	.3444 ± .0031	.3673 ± .0015	.9501 ± .0037	1.02 ± .24
O ₈ ¹	.2976 ± .0031	.5800 ± .0015	.7122 ± .0033	0.99 ± .23
O ₉	.2433 ± .0031	.3072 ± .0014	.5507 ± .0033	1.34 ± .26

¹ Phosphorus oxygens.² Non-octahedrally bonded water.

DISCUSSION OF THE STRUCTURE

The laueite structure is based on an infinite chain of vertex-linked oxygen octahedra, with Fe³⁺ occupying the octahedral centers, the chain oriented parallel to the *c*-axis (Fig. 2). Chains are in turn connected to others 5.28 Å apart by PO₄³⁻ tetrahedra which also bridge through isolated octahedra (with Mn²⁺ as centers) to chains 10.66 Å apart. The ratio ΣO (for oxygens in octahedra):ΣFe, Mn=16:3. This ratio is satisfied by a pattern of isolated octahedron+edge-linked octahedral pair—as in the vivianite structure (Mori and Ito, 1950), Fe₃(PO₄)₂(H₂O)₈, or an infinite chain of vertex-linked octahedra+isolated octahedron—as in laueite. The laueite structural formula is then Mn²⁺Fe₃³⁺(OH)₂(PO₄)₂(H₂O)₆ · 2H₂O, the non-octahedrally bonded waters appearing in a cavity left in the structure. The larger mean Mn-O interatomic distance (Table 3) con-

TABLE 3. INTERATOMIC DISTANCES OF LAUEITE¹

Tetrahedral distances		Octahedral distances			
P-O ₄	1.522	Mn-O ₁	2.068	Fe ₁ -O ₃	1.969
P-O ₆	1.550	Mn-O ₂	2.187	Fe ₁ -O ₄	1.999
P-O ₇	1.537	Mn-O ₆	2.083	Fe ₁ -O ₇	1.981
P-O ₈	1.525		—	Fe ₂ -O ₃	1.916
aver.	1.534 Å	aver.	2.113 Å	Fe ₂ -O ₈	1.964
				Fe ₂ -O ₉	2.103
				aver.	1.989 Å

¹ All ± .03 Å

firms the assumption that Mn resides in the isolated octahedron centered at the origin.

STEREOISOMERISM: POSSIBLE STRUCTURES FOR STEWARTITE
AND STRUNZITE

Since the ligands consist of the unidentate OH^- and H_2O and the tetradentate PO_4^{3-} group, the stereoisomeric nature of the octahedra can now be characterized.

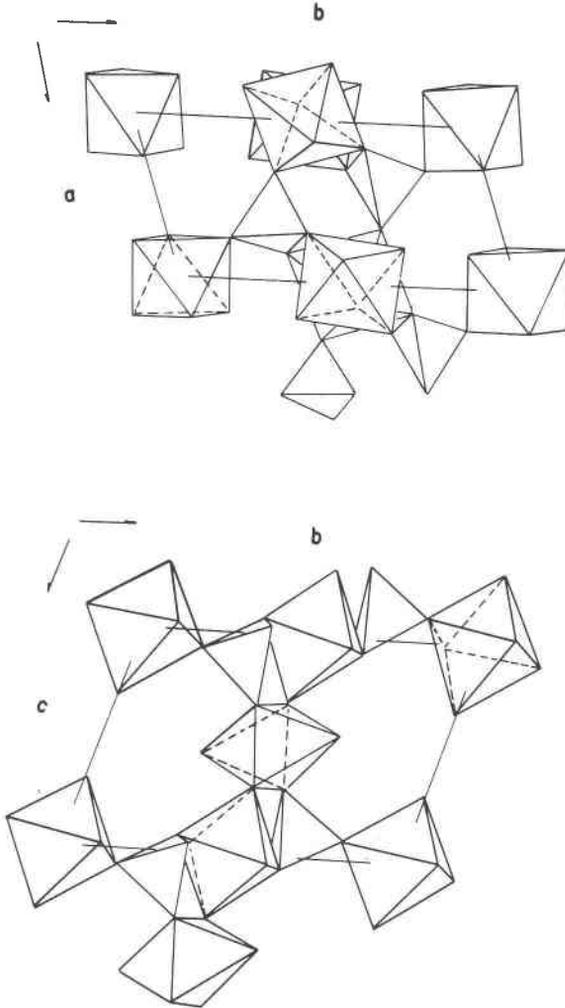
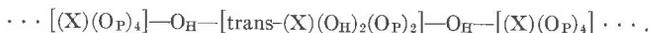


FIG. 2. Representation of structure in ab -plane and bc -plane for laucite. In the upper drawing, octahedron at $a=0$, $b=\frac{1}{2}$ has its center at $0\frac{1}{2}0$; octahedron at $a=1$, $b=\frac{1}{2}$ has its center at $0\frac{1}{2}\frac{1}{2}$.

Setting X for the metal, O_H as either OH^- or H_2O oxygens, and O_P as an oxygen affixed to the PO_4^{3-} tetrahedral group, the isolated octahedron whose coordination center is at the origin of the cell can be specified as $trans-(X)(O_H)_4(O_P)_2$ (Fig. 2) and the chain of octahedra with O_H bridges as

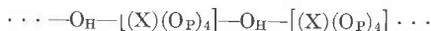


The possibility of a cis-analogue was investigated and a packing model resulted in a cell whose constants and symmetry (Fig. 3) suggest the recently characterized polymorph stewartite¹ (Table 1). The isolated octahedron can be specified as $cis-(X)(O_H)_4(O_P)_2$ and the chain of octahedra with O_H bridges as

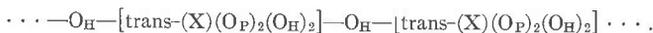


Since $2 \times (Fe^{3+}-O-Fe^{3+}) \sim 8 \text{ \AA}$, which is the chain repeat distance for vertex-linked octahedra, the chains are assumed to be parallel to the c -axis in strunzite (Table 1, Fig. 4). A structural fit can be made assuming two sets of symmetry independent chains in an asymmetric unit of structure with chain I at the origin, and chain II at $a = \frac{1}{2}$, $b = 0$. The octahedra can be specified as

Chain I



Chain II



isolated octahedron at $\frac{1}{4} \frac{1}{4} \frac{1}{2}$

$trans-(X)(O_P)_2(O_H)_4$.

Structure factor calculations were made for the stewartite and strunzite postulated structures, even though the oxygen and phosphorous coordinates are very crude, and compared with powder data. Though the results are encouraging, the final test rests on formal crystal structure analysis. As yet, no good single crystals worthy of structural studies have been located by the author. He will be indebted to anyone who can supply such items.

FURTHER REMARKS

No attempt to differentiate hydroxyl ions from water was made nor were hydrogen atoms located. The location of hydroxyl ions in orthophosphate structures is an interesting problem since many divalent metal orthophosphates can be oxidized without severe damage to the crystal structure. The problem is just which octahedrally bound water molecules in the structure are "hydroxylated." Presently, heating experi-

¹ The superstructure is not considered in the present discussion.

ments are being undertaken in order to prepare trivalent analogues of some hydrated ferrous orthophosphates. Ludlamite, phosphosiderite and Fe-rich hureaulite rapidly convert to the Fe^{3+} end-members upon heating at 160°C . in the presence of air. Powder patterns indicate that the struc-

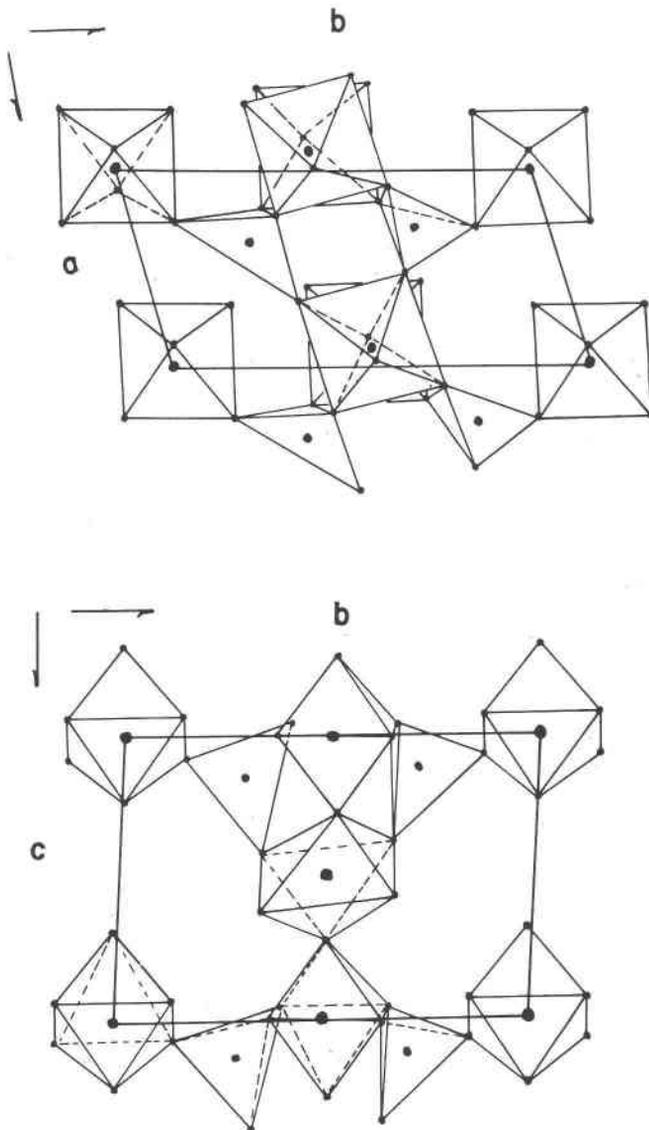


FIG. 3. Representation of possible structure for stewartite. Note lack of inversion center.

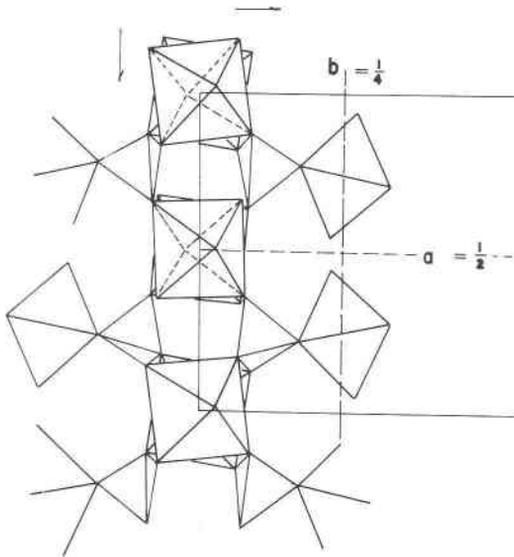


FIG. 4. Representation of possible strunzite structure in ab -plane.

tures remain intact throughout the course of oxidation. Unoxidized ludlamite, for example, is $\text{Fe}_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$ whereas fully oxidized material is $\text{Fe}_3(\text{OH})_3(\text{PO}_4)_2(\text{H}_2\text{O})$. Since only minor structural change has taken place (essentially decrease in cell volume) the roles of water and hydroxyl are inferred to be equivalent, though the oxidized material is probably metastable at room temperature. Vivianite is a hydrated ferrous orthophosphate with all water molecules octahedrally bound as in ludlamite. However, when vivianite is heated in the presence of air at temperatures greater than 112°C ., it suffers decomposition to apparently amorphous material. The results of these studies are the subject matter of an ensuing paper.

At present, laueite is the only example of a vertex-linked chain structure of octahedra among the orthophosphates. The structures of meta-strengite, $\text{FePO}_4(\text{H}_2\text{O})_2$, hureaulite, $\text{H}_2\text{Mn}_5(\text{PO}_4)_4(\text{H}_2\text{O})_4$; and flinkite, $\text{Mn}_2^{2+} \text{Mn}^{3+}(\text{AsO}_4)(\text{OH})_4$ are presently under investigation in this laboratory.

ACKNOWLEDGMENTS

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NOTE

An independent structure determination of laueite was carried out by Drs. K. Plieth, G. Ruban and H. Smolczyk at Technische Universität, Berlin, Germany. It is reported in a recent issue of *Acta Crystallographica*. We agree on interpretation of the structure. Their work was based on two-dimensional projections; this paper gives more accurate results as it was a 3-dimensional study. I am indebted to the above authors for their preprint on laueite.