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THE CRYSTAL STRUCTURE OF METASTRENGITE AND ITS RELATIONSHIP TO STRENGITE AND PHOSPHOPHYLLITE

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ABSTRACT

The crystal structure of metastrengite, $Fe^{3+}(PO_4)(H_2O)_2$, was solved by interpretation of heavy atom vectors on three Patterson projections, by electron density projections, and by three-dimensional least-squares refinements.

The structure consists of linkages of octahedra and PO_4^{3-} tetrahedra. The octahedra are insular and are held together to form a three-dimensional structure by the tetrahedra. As in strengite, the water molecules appear at the ends of an octahedral edge, hence the octahedral structural formula can be written *cis*-$Fe(O_p)_4(O_h)_2$, where O_p is oxygen belonging also to the PO_4^{3-} tetrahedral group and O_h is an oxygen also belonging to a water molecule. Each of the O_p oxygens is associated with one phosphorus center and one iron center.

The major differences in the strengite and metastrengite structures are attibuted to the "tilt" of the tetrahedra. It is further noted that metastrengite-like subcells in the phosphophyllite structure confirm Strunz's suggestion of structural similarities between metastrengite and phosphophyllite.

INTRODUCTION

Metastrengite, $Fe^{3+}(PO_4)(H_2O)_2$, is a common product of hydrothermally reworked triphylite occurring in Li-Fe phosphate bearing pegmatites, a rare mineral in limonite beds, and a constituent of certain soils. It has one known isotype, metavariscite, $Al(PO_4)(H_2O)_2$, and one known dimorph, strengite. Strengite, in turn, has three known isotypes—variscite, $Al(PO_4)(H_2O)_2$; scorodite, $Fe^{3+}(AsO_4)(H_2O)_2$; and mansfieldite, $Al(AsO_4)(H_2O)_2$.

Metastrengite and strengite commonly occur together in pegmatites and are often difficult to distinguish, as both usually occur as rose-pink aggregates or reniform crusts. Metastrengite is monoclinic and strengite is orthorhombic; pertinent data of their structure cells are given in Table 1.

Some reasons for undertaking solution of the metastrengite crystal structure are

(1) to compare it with the structure of strengite, which is known, (2) to test the suggestion of Strunz (1942) that there may exist a structural relationship with phosphophyllite, $Zn_2Fe(PO_4)_2(H_2O)_4$, a recently determined structure, and (3) to add another species to the structural classification scheme of Fe-Mn orthophosphate hydrates as proposed in a previous paper.

Table 1. Cell Data of Metastrengite, Strengite and Phosphophyllite

	Metastrengite	Strengite	Phosphophyllite	
			Kleber Cell	Strunz Cell
a	5.30 Å	10.05	10.23	10.32
b	9.77	9.80	5.08	5.08
c	8.73	8.65	10.49	17.97
β	90°36′	—	120°15′	88°21′
Z	4	8	2	4
S.G.	$P2_1/n$	*Pcab*	$P2_1/c$	$B2_1/d$
Ref.	McConnell (1939)	McConnell (1940)	Wolfe (1940)	Strunz (1942); this study

Table 2. Coordinates and Isotropic Temperature Factors for Metastrengite; Fe-O and P-O Interatomic Distances

	x	y	z	B
Fe	.0916 ± .0005	.8270 ± .0007	.1919 ± .0003	0.59 ± .03
P	−.0867 ± .0008	.1506 ± .0013	.1836 ± .0005	0.70 ± .05
*O_1	.3874 ± .0022	.9494 ± .0028	.1799 ± .0014	2.83 ± .23
*O_2	.0871 ± .0022	.8730 ± .0028	.4275 ± .0014	1.60 ± .18
O_3	.3324 ± .0022	.6814 ± .0027	.2383 ± .0014	1.29 ± .16
O_4	−.1152 ± .0022	−.0066 ± .0035	.1708 ± .0014	1.17 ± .16
O_5	−.2010 ± .0022	.7050 ± .0028	.2178 ± .0014	0.86 ± .15
O_6	.0939 ± .0022	.7873 ± .0028	−.0250 ± .0014	1.63 ± .18

* Water molecules.

Octahedral distances[1]	
Fe-O_1	2.00 Å
Fe-O_2	2.10
Fe-O_3	1.95
Fe-O_4	2.14
Fe-O_5	2.08
Fe-O_6	1.94
Average	2.03 Å

Tetrahedral distances[1]	
P-O_3	1.58 Å
P-O_4	1.58
P-O_5	1.52
P-O_6	1.52
Average	1.55 Å

[1] All distances ±.03 Å.

DETERMINATION OF THE STRUCTURE

The data of McConnell (1939) were confirmed by examining Weissenberg and precession photographs. Metastrengite has four molecules of $Fe^{3+}(PO_4)(H_2O)_2$ in a unit cell of space group $P2_1/n$. Since it is most likely a structure of isolated octahedra (since Σ Fe:Σ 0=1:6) linked to tetradentate PO_4^{3-} tetrahedra, there must be one iron, one phosphorus and six oxygen independent coordinates. The Patterson projections P (uv), P (uw), and P (vw) confirmed the suspicion that all atoms are in general positions.

The *a*- and *c*-axis precession photographs were used for deriving P (uv) and P (vw). Weissenberg photographs of *b*-axis 0-, 1-, 2-, 3-, and 4-levels in three sets each (48, 24 and 8 hour exposures) were prepared using Zr-filtered Mo radiation and a single crystal of dimensions $0.24 \times 0.43 \times 0.43$ mm from Pleystein, Bavaria. From these, 678 independent intensities were collected and estimated visually using a spot scale of 25 units prepared from the crystal. Absorption and $(Lp)^{-1}$ corrections were made using the GNABS program of Burnham (1963). Scattering tables were used for Fe^{2+}, P^{2+}, and O^{-1}, derived from self-consistent field calculations and listed in International Tables, Vol. 3. All computations were done on the IBM 7094 facilities at the Institute of Computer Research, University of Chicago.

The equivalent set of general positions for $P2_1/n$ is x,y,z; $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$ and their inversions. Thus, on P (uv), there will exist a prominent vector somewhere along the line $v=\frac{1}{2}$, related to the Fe atom x-coordinate by $\frac{1}{2}\pm 2x=u$. Likewise, on the line $u=\frac{1}{2}$, we have a peak occurring at $\frac{1}{2}\pm 2y=v$, where u and v are coordinates in Patterson space. The same holds for P (vw); at $v=\frac{1}{2}$, a peak at $\frac{1}{2}\pm 2z$ defines the possible Fe z-coordinates. The possible solutions thus derived from the Patterson projections are $x=\pm.090$, $y=\pm.161$, $z=\pm.183$.

Concentrating now on the xz-projection, the two possible combinations of symmetry independent Fe coordinates are (.090, .183) or (.090, −.183). A rough trial set of structure factor calculations favored the former. The P (uw) map (Fig. 1) reveals the vector $Fe_{xz}-Fe_{\frac{1}{2}-x,\frac{1}{2}-z}$ (labelled "B") and the phosphorus coordinates were derived from vectors "A" ($Fe_{xz}-P_{\frac{1}{2}-x,\frac{1}{2}-z}$) and "C" ($Fe_{xz}-P_{xz}$). Rough structure factor calculations confirmed the phosphorus coordinates (−.085, .189) and the signs thus derived from the Fe and P coordinates were applied to the observed structure factors. Only four oxygen atoms appeared on the electron density map, but the other two could be located by assuming an octahedral oxygen configuration about the iron atom. Three more electron density maps resulted in $R_{h0l}=0.20$. The label "D" on P (uw) corresponds to the contributions of the $Fe_{xz}-(O_{xz}^2, O_{xz}^6)$ vectors.

The possible Fe coordinates are (.090, .161, .183) or (.090, −.161, .183). The latter was chosen after some trial structure factor calculations.

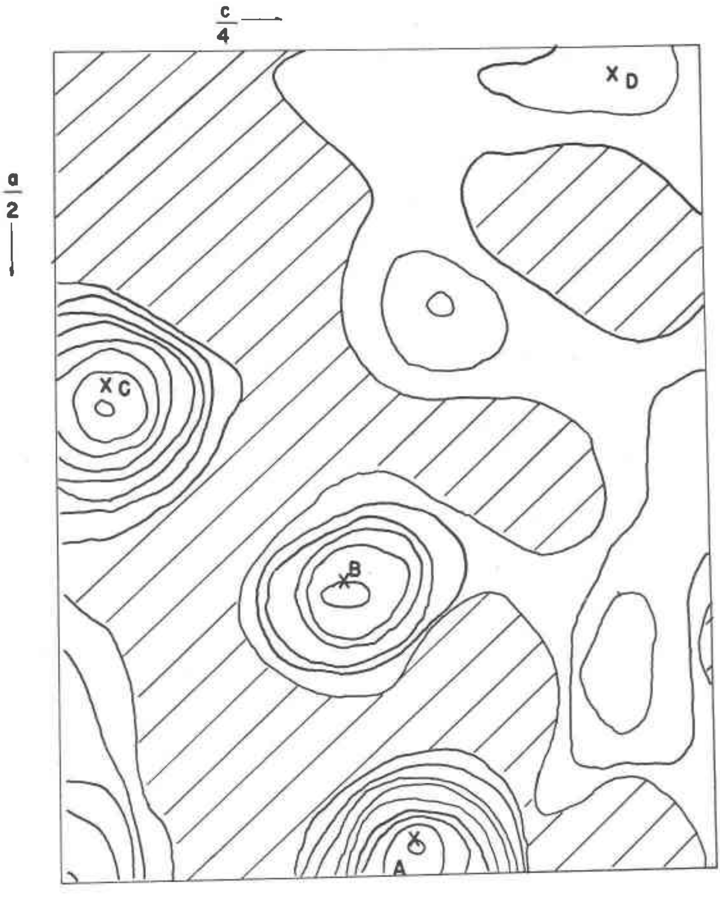

FIG. 1. P (uw) of metastrengite.

Assuming interatomic distances of Fe−O∼2.00 Å and P−O∼1.54 Å, the y-coordinates of the remaining atoms were calculated, two structural configurations being possible. A three-dimensional three-cycle least squares refinement (Busing *et al.* 1963) on the favored configuration with fixed temperature factors (B set to 1.0) and using all collected reflections resulted in $R_{hkl}=0.22$. Inspection of the individual structure factors showed almost consistently $|F_{obs}|-|F_{calc}|$ less than 0 for the strong low-angle reflections. This could be due either to extinction errors or non-linearities in the intensity scale or both. Omission from refinement of 21 of the strongest intensities resulted in $R_{hkl}=0.20$ after one more cycle. Further refinement, now with fixed coordinates and varying temperature factors resulted in $R_{hkl}=0.17$. After three more cycles, varying coordinates and isotropic temperature factors, $R_{hkl}=0.156$. Final inspection of all the employed structure factors showed no gross disparities between those observed and those calculated. The F_{obs} and F_{calc} structure factor tables can be obtained upon request.

DISCUSSION OF THE STRUCTURE

The metastrengite structure consists of isolated metal-centered oxygen octahedra linked together via PO_4^{3-} tetradentate tetrahedra to form a three-dimensional edifice. Two water ligands are associated with each octahedron, the octahedral configuration being *cis*-$Fe(O_p)_4(O_h)_2$, where O_p is oxygen also associated with the PO_4^{3-} groups and O_h is oxygen also associated with a water molecule. Each PO_4^{3-} oxygen is associated with only one P atom and one Fe atom. Figure 2 is a *b*-axis projected polyhedral diagram showing one octahedron (the asymmetric unit of structure), its four associated PO_4^{3-} tetrahedra, and the remaining PO_4^{3-} tetrahedra in the unit cell.

Relation to the Strengite Dimorph. The metastrengite structure is very similar to the strengite structure. Both are *cis*-$Fe(O_p)_4(O_h)_2$ structures (Fig. 3). The coordinates of the strengite structure are from Hiriyana and Sakurai (1949). The notable differences are the more "open" disposition of the tetrahedra about the octahedron in metastrengite (explaining the lower density of this mineral) and the order of the tetrahedral groupings about the octahedron. In each of the *cis*-structures, there are two octahedral faces which have three PO_4^{3-} oxygens at the vertices. Furthermore, in both structures, for the projections chosen, the tetrahedra point either up (solid lines) or down (dashed lines). For the two faces of concern on the metastrengite octahedron, the associated tetrahedra point *down-down-up*. For strengite, they point *down-down-up* and *down-down-down*.

It is now evident that strengite and metastrengite are stereoisomers of each other, even though the order of the ligand species is the same about the octahedral asymmetric unit. The difference, however, is in the "tilt" or "twist" of the PO_4^{3-} ligands.

It is interesting to speculate as to whether a trans- array of tetrahedra could exist about an octahedron with the possibility of a third hypotheti-

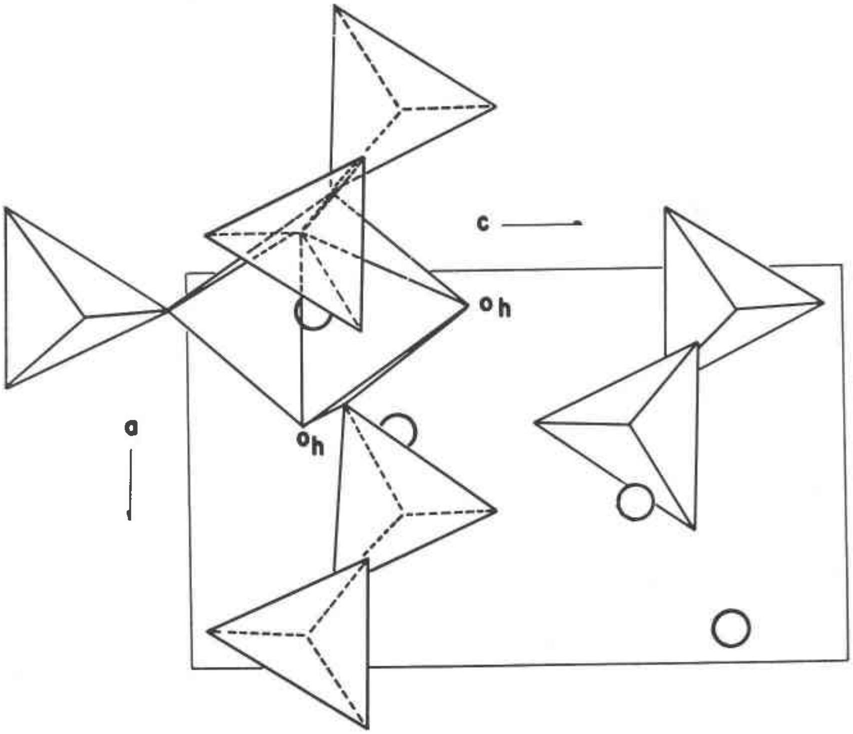

FIG. 2. Metastrengite crystal structure projected on ac-plane. One octahedron (an asymmetric unit of structure), the PO_4^{3-} tetrahedral environment, and the remaining tetrahedra in the cell are shown. The H_2O oxygens are specified; the circles represent Fe atoms.

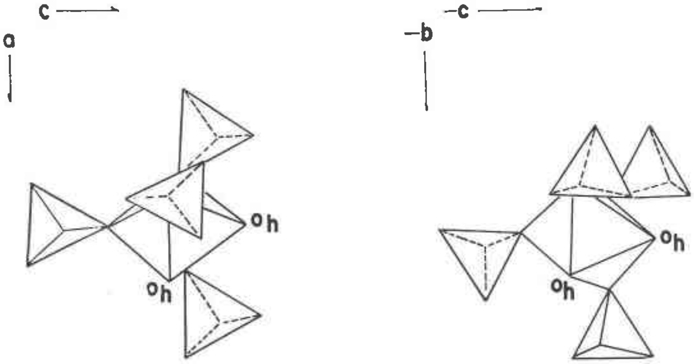

FIG. 3. Environment of tetrahedra and H_2O groups about octahedron in metastrengite (left) and strengite (right).

cal polymorph. The tetrahedra would form a "girdle" about the octahedron and crude models show that such tetrahedra and octahedra can fit nicely. However, with two molecules of water on *opposing* octahedral vertices, there results a more open structure. This is because the tetrahedra sterically hinder any reasonable packing of the ends occupied by water molecules. To better facilitate packing of such octahedra, the open ends (the positions of the water molecules) would have to become fused to form chains of octahedral structure as in laueite (Moore, 1965). In that arrangement, the tetrahedral groups would zigzag up this chain, connecting neighboring octahedral links and cross-linking to other similar chains. Laueite often occurs in close association with strengite and metastrengite indicating that configurations of chains of octahedra as well as isolated octahedral groups can arise in very similar environments.

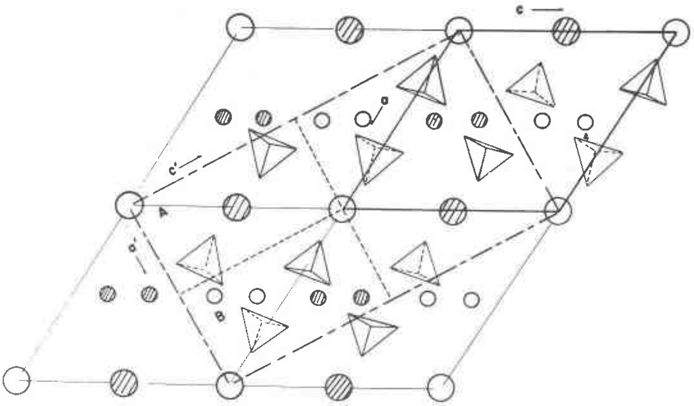

FIG. 4. The phosphophyllite structure. Four Kleber cells each of dimensions $a \times c$ are shown. The long- and short-dash cell is the B-centered cell of Strunz with dimensions $a' \times c'$. The two metastrengite-like cells A and B are denoted by short dashes. Large circles are iron atoms and small circles are zinc atoms. Hatch marks denote operation of the inversion center.

The name redondite for ferrian "variscite" was resurrected by Čech *et al.* (1962). This mineral was originally named by Shepard (1869) and work by Čech *et al.* suggests redondite to be another polymorph of $AlPO_4(H_2O)_2$. Further studies on this material would be most informative.

Relation to Phosphophyllite, $Zn_2Fe^{2+}(PO_4)_2(H_2O)_4$. We turn now to the possibility of a structural relationship between metastrengite and phosphophyllite. Figure 4 shows a *b*-axis projection of the phosphophyllite structure, $2[Zn_2Fe(PO_4)_2(H_2O)_4]$, $P2_1/c$, $a=10.23$, $b=5.08$, $c=10.49$ Å, $\beta=120°15'$ as determined by Wolfe (1940) and used in the structure analysis of Kleber *et al.* (1961). Four cells of the Kleber structure are shown, and the B-face centered cell of twice the area (Strunz, 1941) is sketched in. This cell has the dimensions $a'=10.32$ and $c'=17.97$ Å, each nearly twice the dimensions of the metastrengite *a*- and *c*-axes. The Strunz cell is further partitioned into sub-cells A and B, each approximately of metastrengite dimensions. Cell A contains two PO_4^{3-} tetrahedra whose centers closely resemble x, z and $\bar{x}$, $\bar{z}$ coordinates associated with the phosphorus atoms and the O_p oxygen atoms in metastrengite. Cell B contains the remaining atoms with $\frac{1}{2}-x, \frac{1}{2}-z$ and $\frac{1}{2}+x, \frac{1}{2}+z$ coordinates, and, furthermore, contains zinc atoms strung along the cell diagonal. In metastrengite, these zinc coordinates resemble those of iron, which are somewhat displaced from the diagonal. The zinc in phosphophyllite is in a distorted O_p tetrahedron. Further analogy breaks down when water and iron in phosphophyllite are considered, as these atoms are associated with octahedra centered at 00, $\frac{1}{4}\frac{1}{4}$, and $\frac{1}{2}\frac{1}{2}$ positions in the Strunz cell and are not present in metastrengite. It is interesting to note that the y-coordinates of P, the O_p oxygens, and Zn, as determined by Kleber *et al.* (1961) bear similarity to those for P, O_p oxygens and Fe in metastrengite. The similarity in coordinates as well as the existence of pseudocells in phosphophyllite made up of pieces of metastrengite-like structure explain the similarity in powder data of the two minerals, as noted by Strunz.

CONCLUSIONS

Metastrengite is a *cis*-structure as is strengite, though more open. Though the ligands in the two species are in the same order, they tilt differently, thus affecting packing of the tetrahedra and octahedra. The similarity of the metastrengite structure to that of phosphophyllite is due to similarities in the packing of the PO_4^{3-} tetrahedra as well as the position of the Zn atoms (in phosphophyllite) and Fe atoms (in metastrengite). The arrangement is such that subcells of phosphophyllite bear striking similarity to pieces of the metastrengite structure.

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