

Metavivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, a New Mineral¹

CHARLES RITZ

Department of Chemistry,

ERIC J. ESSENE, AND DONALD R. PEACOR

*Department of Geology and Mineralogy,
The University of Michigan, Ann Arbor, Michigan 48104*

Abstract

Metavivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, is a new mineral occurring with kryzhanovskite in solution cavities in triphylite at the Big Chief pegmatite near Glendale, South Dakota. It is triclinic, with $a = 7.81 \text{ \AA}$, $b = 9.08 \text{ \AA}$, $c = 4.65 \text{ \AA}$, $\alpha = 94.77^\circ$, $\beta = 97.15^\circ$, $\gamma = 107.37^\circ$, and is isostructural with symplepsite, $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$. Electron probe analysis indicates that it is a polymorph of vivianite. Vivianite and parasymplepsite are therefore isostructural, monoclinic dimorphs of the isostructural and triclinic minerals metavivianite and symplepsite.

Introduction

The pegmatites of the Black Hills, South Dakota, are well known as sources of a variety of primary and secondary phosphates. In 1969, Dr. David Garske of the South Dakota School of Mines kindly donated to us specimens of phosphate minerals which are products of the alteration of triphylite. Crystals from one of these specimens were used in a single-crystal study, with preliminary results indicating that they were triclinic, and similar to symplepsite, $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$. However, chemical analysis indicated the presence of P but no As.

Symplepsite is the triclinic dimorph of monoclinic parasymplepsite. The mineral vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, is isostructural with parasymplepsite (Mori and Ito, 1950). Our preliminary results thus indicated that our specimens were a dimorph of vivianite and related to that mineral as symplepsite is to parasymplepsite. Detailed examination has verified this relationship. The name metavivianite has been chosen to emphasize the dimorphous relationship to vivianite, as with the phosphates (meta)vauxite and (meta)strengite. The nature of the existing names for the two related arsenates unfortunately precludes a choice of names which would more clearly illustrate the isostructural relations between

the two phosphates and the two arsenates. Type material of metavivianite is present in the collections of the U. S. National Museum (Smithsonian Institution) and the Department of Geology and Mineralogy, The University of Michigan. The mineral and the name have been approved by the I.M.A. Commission on New Minerals and Mineral Names.

Occurrence

The mineral occurs on one specimen collected at the Big Chief pegmatite mine, one half mile south of Glendale, Pennington County, South Dakota ($43^\circ 52.3' \text{ N}$, $103^\circ 22.1' \text{ W}$). Phosphates from this locality have been described by Roberts and Rapp (1965). Crystals of primary triphylite, some measuring up to 6 feet in diameter, have been altered by late-stage pegmatitic solutions. Secondary minerals are abundant and include ludlamite, hureaulite, beraunite, rockbridgeite, laueite, heterosite-purpurite, and strunzite.

The metavivianite occurs on a specimen of massive triphylite containing veinlets of spessartine-rich garnet, pyrrhotite, sphalerite, and quartz. The surface of the triphylite is pitted with solution cavities up to 1 mm in diameter which generally follow the traces of cleavages. The metavivianite occurs in the solution cavities, intimately intergrown with dark red kryzhanovskite. The identity of the latter mineral was established using single-crystal diffrac-

¹Contribution No. 318 from the Mineralogical Laboratory, Department of Geology and Mineralogy, The University of Michigan, Ann Arbor, Michigan 48104.

tion ($a = 8.26 \text{ \AA}$, $b = 10.12 \text{ \AA}$, $c = 9.37 \text{ \AA}$, space group $Pcnb$) and qualitative microprobe analysis, with comparison with the data of Moore (1971). Kryzhanovskite is the only mineral observed to be in an apparent equilibrium relationship with metavivianite, although hureaulite is present in some other cavities.

Physical Properties

Metavivianite occurs as flat, prismatic crystals, elongated along c , and with principal form $\{110\}$. Some crystals having more regular cross-sections are striated parallel to c . There is a perfect (110) cleavage. The color is leek-green. Most crystals are opaque to translucent, but small grains are transparent. The specific gravity was not measured due to the small size of the crystals and the presence of impurities. The calculated density is 2.69 gm/cm^3 .

Optical properties of metavivianite are generally similar to those of vivianite. By direct measurement, $2V_z$ is $+ 85 \pm 5^\circ$. Indices of refraction are $\alpha = 1.579 \pm 0.006$, $\beta = 1.603 \pm 0.002$ and $\gamma = 1.629 \pm 0.002$. The relation between the optical directions and cleavage is $X \perp (110)$, $YZ \parallel (110)$. The pleochroic formula is $X > Z > Y$, with $X =$ light-blue to blue-green, $Y =$ yellow-green to light green, $Z =$ yellow to light green. The pleochroic colors are presumably intensified by oxidation of the iron, but the physical properties were measured on light-colored grains.

Crystallography

Single crystals were studied using Weissenberg and precession methods. Unit-cell parameters are $a = 7.81(2) \text{ \AA}$, $b = 9.08(2) \text{ \AA}$, $c = 4.65(1) \text{ \AA}$, $\alpha = 94.77(10)^\circ$, $\beta = 97.15(10)^\circ$, $\gamma = 107.37(10)^\circ$. The space group is $P1$ or $P\bar{1}$. X-ray photographs showed the presence of two twinned lattices. The crystals are twinned on $\{110\}$. Wolfe (1940) showed that the lattices of the monoclinic members of the vivianite group (parasymplekite was not recognized at that time) are closely related to the lattices of the triclinic phases (e.g., symplekite). The twin plane $\{110\}$ of the triclinic phases is structurally equivalent to the true mirror plane (010) in the monoclinic phases. We have verified this relation by comparing photographs of untwinned vivianite and twinned metavivianite. Twinning was not observed optically.

Data from an $\text{FeK}\alpha$ powder photograph are listed in Table 1. Calculated interplanar spacings and indices were obtained using lattice parameters from

TABLE 1. X-Ray Powder Data for Metavivianite*

hkl	d_{cal} (Å)	d_{obs} (Å)	I	hkl	d_{cal} (Å)	d_{obs} (Å)	I
010	8.60	8.59	40	211	2.78	2.77	30
110	6.73	6.71	100	221	2.77		
110	4.89	4.86	40				
011	4.27	4.27	10	201	2.67	2.67	5
111	3.88	3.87	30	131	2.60	2.60	10
210	3.85			310	2.58		
111	3.71	3.72	2	320	2.49	2.50	10
010	3.64	3.63	2	121	2.48	2.48	2
				300	2.45	2.46	2
111	3.08	3.07	10			1.743	5
210	3.06					1.631	10
130	3.01	3.00	5			1.503	2
021	2.95	2.95	5			1.456	10
121	2.91	2.90	20			1.341	2
						1.309	2

*FeK Mn-filtered radiation. Camera radius 57.3 mm. Intensities visually estimated. There are a number of additional, very weak lines with d-values less than 1.3 Å.

the single-crystal study. One other line not listed in Table 1 with a spacing of 3.47 Å appeared on the photographs. This was not indexable using the metavivianite unit cell, but since it varied in intensity from 2 to 30 on different photographs, and since some impurity was present in all X-rayed samples, it is assumed to be due to an impurity.

As expected for two isostructural compounds, the patterns of symplekite and metavivianite are similar. The larger interplanar spacings for symplekite, relative to corresponding lines for metavivianite, result in clear differences between the patterns. The patterns for vivianite and metavivianite are also similar, as expected from their structural similarity. The patterns of each have unique features with respect to the first peak at approximately 8 Å.

Chemical Analysis

A specimen of metavivianite and a vivianite from an unknown locality were analyzed using the electron microprobe. The results are listed in Table 2. The metavivianite is very similar to the vivianite, both phases having essentially the same wt/percent ratios of Fe/Mn, approximately 10:1. Only traces of other elements are present in the metavivianite. There is less than 0.1 percent As since it was not detected using repeated, slow spectrometer scans. The slightly high totals of wt/percent oxides and cations sums are probably due to oxidation of part of the iron and concomitant loss of some water. We conclude that metavivianite and the vivianite are nearly identical in composition for the elements

TABLE 2. Chemical Analyses

Wt Percent oxides	Metavivianite	Vivianite	Fe ₃ (PO ₄) ₂ ·8H ₂ O
FeO	38.9	37.7	43.0
MnO	4.2	3.5	---
NiO	0.13	0.6	---
CuO	<0.05	0.14	---
ZnO	<0.05	1.5	---
CaO	0.5	<0.06	---
Na ₂ O	<0.07	0.8	---
P ₂ O ₅	28.4	28.0	28.3
As ₂ O ₅	<0.1	<0.1	---
H ₂ O	(28.7)	(28.7)	28.7
sum	100.8	100.9	100.0
Cations for 8 oxygens (atomic basis)			
Fe	2.71	2.63	3.00
Mn	0.30	0.25	---
Ni	0.01	0.04	---
Cu	---	0.01	---
Zn	---	0.09	---
Ca	0.05	---	---
Na	---	0.13	---
P	2.00	1.97	2.00
O	8.00	8.00	8.00
H ₂ O	(8.00)	(8.00)	8.00
sum cations	5.06	5.12	5.00

*Microprobe standards used: Fe-Binns ilmenite, Mn-Broken Hill rhodonite, Ni-synthetic NiAl₂O₄, Cu-Cu metal, Zn-Zincian calcite, Ca-Calcite, Na-Amelia albite, P-Black Hills triphylite.

Operating conditions: 0.006 μa sample current on calcite.

Corrections: using Rucklidge's EMPADR VII program (J. Rucklidge and E.L. Gasparri, Dep. of Geology, Univ. Toronto, written. comm., 1969)

with $Z < 10$ and therefore by analogy with vivianite, the formula of metavivianite is $(\text{Fe}, \text{Mn})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$.

Infrared Spectrum

The infrared absorption spectra, shown in Figure 1 for vivianite and metavivianite, were obtained with a Beckmann IR-12 using the fast scan mode.

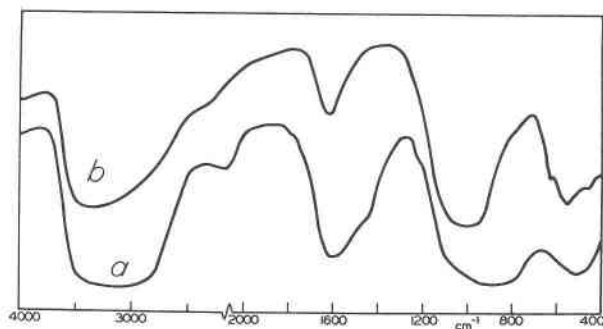


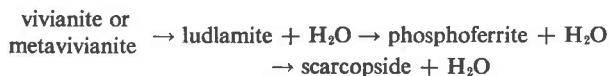
FIG. 1. Infrared absorption spectra of metavivianite (a) and vivianite (b).

The samples were imbedded in KBr pellets. A spectrum of KBr blank showed no absorption above 400 cm^{-1} , and no noticeable lines due to absorbed H_2O . The spectra of vivianite and metavivianite show broad absorptions around the regions of 3400, 1600, 900, and 500 cm^{-1} . The first two broad peaks indicate the presence of water, and the last two peaks are characteristic of PO_4^{3-} . The qualitative spectra indicate the similarity in composition and crystal structure of vivianite and metavivianite.

Discussion

Metavivianite and vivianite are members of a series of hydrated iron phosphates: $\text{Fe}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$, which includes phosphoferrite ($n = 3$), ludlamite ($n = 4$), and anhydrous sarcopsite (Moore, 1971).² All these minerals show substantial solid solution with Mn, and are easily oxidized to Fe^{3+} with loss of H^+ .

The members of this series are related by simple reactions with increasing temperature:



The coexistence of metavivianite and kryzhanovskite (the oxidized equivalent of phosphoferrite) may be due to the solid solution of Mn and the potential for oxidation, or it may represent a disequilibrium assemblage. If metavivianite-kryzhanovskite is an equilibrium assemblage, then *some* oxidized Mn-bearing ludlamite of equivalent composition cannot be stable at the same conditions. Moore (1971) has also argued for the persistent stability of the series phosphoferrite-kryzhanovskite and the relative instability of crystalline ferric equivalents based on crystal-chemical and structural considerations.

The P - T relationships of vivianite and metavivianite are unclear. Insufficient data are available on vivianite and metavivianite solid solutions to infer which has the larger cell volume for the same composition. Since these polymorphs have substructural elements in common, the free energy differences are probably small. The formation of a specific polymorph may be controlled by non-equilibrium factors rather than P - T - X variables.

² Moore (written communication, 1973) informs us of the existence of still another iron phosphate hydrate with $n = 1$.

References

- MOORE, P. B. (1971) The $\text{Fe}^{2+}_3(\text{H}_2\text{O})_n(\text{PO}_4)_2$ homologous series: crystal-chemical relationships and oxidized equivalents. *Am. Mineral* **56**, 1-17.
- MORI, H., AND T. ITO (1950) The structure of vivianite and symplectite. *Acta Crystallogr.* **3**, 106.
- ROBERTS, W. L., AND G. RAPP (1965) *Mineralogy of the Black Hills*. Espe Printing Co., Rapid City, South Dakota.
- WOLFE, C. W. (1940) Classification of minerals of the type $A_3(\text{XO}_4)_2 \cdot n\text{H}_2\text{O}$. *Am. Mineral.* **25**, 787-809.

Manuscript received, December 6, 1973; accepted for publication, April 19, 1974.