

Mahlmoodite, $\text{FeZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, a new iron zirconium phosphate mineral from Wilson Springs, Arkansas

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ABSTRACT

Small (<0.5 mm) cream white spheres observed in V ore from the Union Carbide mine at Wilson Springs, Garland County, Arkansas, have been identified as ferrous zirconium phosphate tetrahydrate, $\text{FeZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. This new mineral, named mahlmoodite, occurs as spherules of radiating fibers usually perched on crystals of pyroxene in vugs. The X-ray powder diffraction data, which are analogous to those of synthetic $\alpha\text{-MZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ where M is a divalent cation Mn, Ni, Co, Cu, or Zn, have been indexed on a monoclinic lattice in space group $P2_1/c$. The refined unit-cell dimensions are $a = 9.12(2) \text{ \AA}$, $b = 5.42(1) \text{ \AA}$, $c = 19.17(2) \text{ \AA}$, $\beta = 94.8(1)^\circ$; $Z = 4$. Density (calc.) is 2.877 g/cm^3 . The strongest powder lines are (hkl), d , I : (002), 9.58, 75; ($\bar{1}11$), 4.572, 65; ($\bar{1}04$), 4.382, 80; (104), 4.092, 60; (204), 3.160, 100; (310), 2.640, 70. The soft, lathlike fibers have optically negative refractive indices $\beta = \gamma = 1.650$ in the plane of the laths, and $\alpha < 1.646$.

INTRODUCTION

In a study of the unusual mineral assemblages of the Union Carbide V ore deposit at Wilson Springs, Garland County, Arkansas (approximately 10 km west of the Magnet Cove alkaline igneous complex), small, creamy white spheres were found, less than 0.5 mm diameter, usually perched on greenish black sodic pyroxene crystals in vugs (Fig. 1). This mineral was first noted and correctly formulated by Hey et al. (1982), who illustrated the spherules perched on groups of kolbeckite ("eggonite," $\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$) plates. The mineral always appears to be the last to be deposited in the cavities where it occurs. We have found these spherules to be a ferrous zirconium phosphate, a previously unknown mineral species, and have given it the name mahlmoodite. This name has been approved by the International Mineralogical Association Commission on New Minerals and Mineral Names. Several micromount specimens of mahlmoodite have been deposited with the Smithsonian Institution, Washington, DC.

The geological and mineralogical relations of the Union Carbide Corporation Vanadium mine at Wilson Springs have been described by Stewart Hollingsworth (Stone et al., 1982). The mine is located in a contact region between the alkalic igneous rocks of the Potash Sulfur Springs intrusives and the surrounding sedimentary rocks.

Mahlmoodite is named for the late Bertha K. Mahlmoed, for many years Administrative Assistant of the Branch of Analytical Laboratories, U.S. Geological Survey. Her career was distinguished by unstinting helpfulness to all who knew her, and in honoring her we also acknowledge the indebtedness of Survey scientists to their

devoted nonprofessional assistants, both technical and clerical.

PHYSICAL PROPERTIES OF MAHLMOODITE

In cross section (Fig. 1), the spherules consist of thin, flat, radiating, optically homogeneous crystals of the new mineral. The lathlike plates (<0.05 mm in maximum length) show parallel extinction and positive elongation. The crystals exhibit very low birefringence and are effectively uniaxial negative; the pseudoordinary index $\beta = \gamma = 1.652 \pm 0.002$. The flakes were too small to be mounted on a spindle stage, but examination of fragments of the spherule shows that the index normal to the plate $\alpha < 1.646$.

The spherules usually contain a core of loose material approximately one-third to one-half the radius of the sphere (Fig. 1). Energy-dispersive X-ray spectra indicated a composition similar to that of the surrounding mahlmoodite, but with considerably higher amounts of Si. No optical or X-ray information could be obtained for this core material.

The mahlmoodite fibers are soft, with hardness ~ 3 . The density could not be measured; the density calculated from the unit-cell content of four formula units (Table 1) is 2.877 g/cm^3 . The average index of refraction based on this density and the molar refractivities of Mandarino (1976) according to the Gladstone-Dale law is 1.650.

X-RAY POWDER DATA AND CRYSTALLOGRAPHY

A single bundle of fibers was used to obtain a pattern in a Gandolfi camera using $\text{CrK}\alpha$ radiation ($\lambda = 2.291 \text{ \AA}$). Reflections were recorded to $d = 1.52 \text{ \AA}$, but subsequent indexing procedures were confined to 15 sharp lines up to $2\theta = 70^\circ$ ($d = 2.0 \text{ \AA}$). A search for a match to these

† Deceased October 4, 1990.

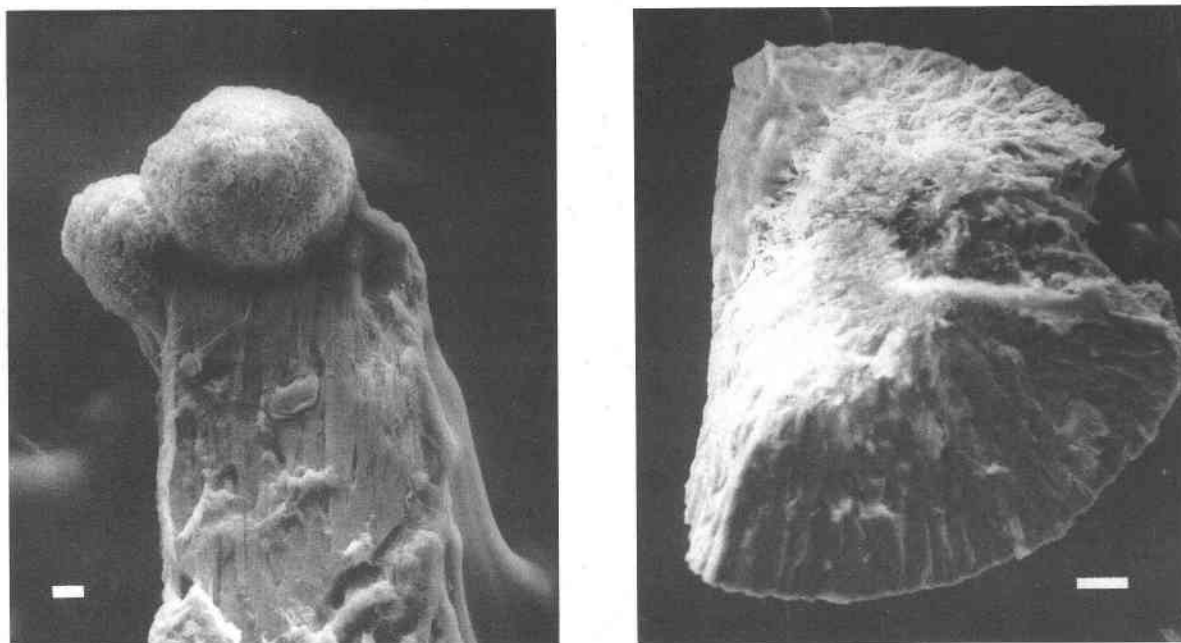


Fig. 1. Scanning electron micrograph of mahlmoodite spherules: (left) on augite; (right) section of broken spherule showing radiating fibers of mahlmoodite around a core of unknown constitution. Bars represent 10 μm .

data did not lead to any iron zirconium phosphate mineral but did reveal a resemblance to a series of compounds of the type $\text{MZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ with $\text{M} = \text{Mn, Ni, Co, Cu, and Zn}$ (but not Fe) studied by Alluli et al. (1976). The marked similarity of the powder patterns of mahlmoodite to the published patterns for these compounds is shown in Figure 2. Alluli et al. (1976) did not attempt to index their patterns; therefore no unit cells were determined, but their synthetic samples were chemically well characterized. They each conform to the general formula given above, and it is natural to conclude that the new mineral corresponds to the Fe member of the group, with the formula $\text{FeZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$.

To determine a unit cell from our powder data, much reliance was placed on the work of Clearfield and his

coworkers. They reported crystal structure analyses of $\text{KHZr}(\text{PO}_4)_2$ (Clearfield et al., 1984), $\text{H}_2\text{Zr}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (Troup and Clearfield, 1977), and $(\text{NH}_4)_2\text{Zr}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (Clearfield and Troup, 1973). In all these structures they

TABLE 1. Crystallographic data for mahlmoodite and analogous synthetic compounds $\text{MZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$

M	a (Å)	b	c	β (°)	(2 θ)*
Iron mahlmoodite**	9.112(6)	5.412(7)	19.19(1)	94.81(6)	0.057
Mn†	9.23(7)	5.36(7)	19.32(10)	95.0(7)	0.23
Co	9.12(4)	5.37(3)	19.26(4)	94.8(3)	0.08
Ni	9.14(1)	5.31(1)	19.20(2)	95.2(1)	0.03
Cu	9.04(1)	5.39(1)	19.23(2)	95.8(1)	0.03
Zn	9.12(4)	5.39(3)	19.24(4)	95.9(3)	0.09

Monoclinic, space group $P2_1/c$; $Z = 4$.

* Standard deviation of 2θ from least-squares analysis of powder data.

** Derived by least-squares analysis of data from Table 1. Thirteen uniquely indexed lines with $d > 2.0$ Å were used in the analysis.

† These and following unit cells are derived from least-squares analysis of d -value data of Alluli et al. (1976); seven or eight uniquely indexed lines out of 13 to 15 lines listed with $d > 2.5$ Å were used in the analyses.

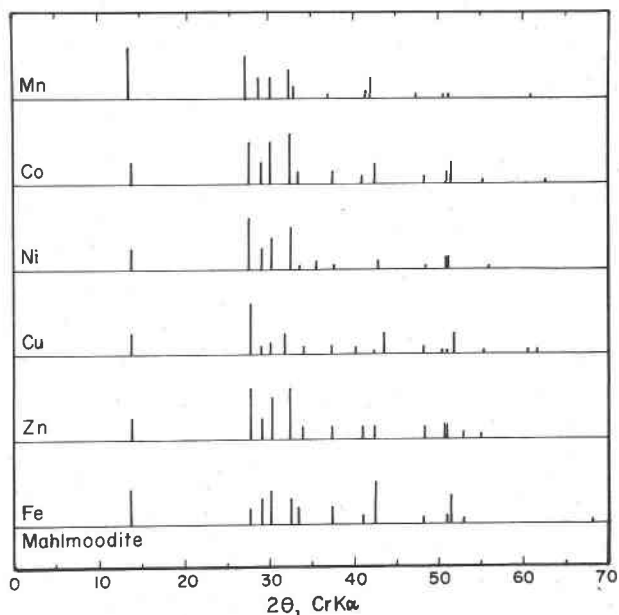


Fig. 2. Schematic representation of powder patterns of mahlmoodite and synthetic analogues based on 2θ values for $\text{CrK}\alpha$ radiation derived from d values given by Alluli et al. (1976). The first line at the left (~ 9.6 Å) is the 002 reflection, corresponding to the interlayer spacing.

TABLE 2. X-ray powder diffraction data for mahlmoodite

<i>hkl</i>	d_{obs}	d_{calc}^*	I^{**}
002	9.58	9.559	75
004	4.780	4.779	35
$\bar{1}11$	4.572	4.563	65
$\bar{1}04$	4.382	4.384	80
104	4.092	4.090	60
202	3.978	3.974	40
014	3.574	3.582	40
114	3.266	3.263	20
204	3.160	3.162	100
$\bar{3}04$	2.661	2.660	20
215		2.659	
310	2.640	2.642	70
116	2.574	2.577	15
208	2.046	2.045	15
	1.999		20
	1.990		25
	1.783		20
	1.738		15
	1.706		20
	1.663		10
	1.580		15
	1.523		20

* The d values calculated from refined unit cell given in Table 1.

** Intensities normalized from values estimated from peak heights on a densitometer trace of the Gandolfi films, made with a Nonius Model II microdensitometer.

found a common $[\text{Zr}(\text{PO}_4)_2]^{2-}$ layer component, which is pseudohexagonal and has orthorhombic dimensions $a = 9.2 \text{ \AA}$ and $b = 5.3 \text{ \AA}$ in the various monoclinic structures (see below). The c axis corresponds to the interlayer spacing, and the 002 reflection is always prominent at low 2θ angles. Thus the problem of indexing our powder data was simplified by predetermined a^* , b^* , and c^* values and was reduced to finding the appropriate value of β^* . Tests with $\beta^* \sim 77^\circ$, analogous to that of the compound $(\text{NH}_4)_2\text{Zr}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (Clearfield and Troup, 1973) did not succeed, but by trial it was found that, with $\beta^* \sim 85^\circ$, a satisfactory indexing could be achieved. The refined unit-cell data are given in Table 1. The measured and calculated powder data for mahlmoodite are given in Table 2.

With this result as a starting point it was possible also

TABLE 3. Electron microprobe analysis of mahlmoodite

	Wt%*	Mole ratios**	
P_2O_5	36.2(9)	2.01	2.01
ZrO_2	28.7(6)	0.91	
TiO_2	0.7(1)	0.03	0.96
Al_2O_3	0.3(1)	0.02	
FeO	16.1(8)	0.88	1.07
MnO	0.8(2)	0.04	
CaO	1.3(5)	0.09	
MgO	0.26(6)	0.03	
Na_2O	0.11(5)	0.03	
SiO_2	0.3(2)	0.02	
F	0.5(2)		
$\text{H}_2\text{O}^\dagger$	(14.7)	3.2	
TOTAL	(100.0)		

* Average of 25 analyses; standard deviations in terms of last significant figure in parentheses.

** Mole ratios of the cations; SiO_2 , F excluded from formula ratios.

† H_2O by difference; probably reduced by vacuum.

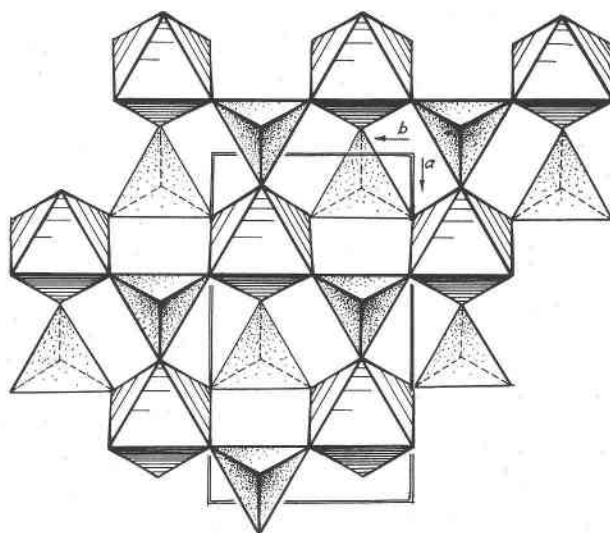


Fig. 3. Schematic representation of the proposed diphosphozirconate $[\text{Zr}(\text{PO}_4)_2]_n$ layer structure in mahlmoodite, by analogy with $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (Clearfield and Smith, 1969). The pseudohexagonal linkage of PO_4 tetrahedra (stippled) and ZrO_6 octahedra (line-shaded) is shown with the monoclinic cell base.

to index the more rudimentary d -value data of Alluli et al. (1976) for the five other divalent cations. Table 1 gives the unit-cell data and unit cells that we obtained by refinement of the d -value data published for the other cationic analogues by Alluli et al. (1976). A schematic comparison of the powder data for mahlmoodite and powder data reported by Alluli et al. (1976) is shown in Figure 2.

CHEMISTRY OF MAHLMOODITE

Energy-dispersive X-ray spectra obtained with a scanning electron microscope show major Zr and P, moderate Fe, and minor Ca, Si, and Ti. Because of the small size and scarcity of the spheres, it was not possible to determine chemical composition by macroscopic means. Initially, X-ray powder data (Fig. 2) provided substantial information about its formulation, by analogy with powder data for isomorphous phases (Alluli et al., 1976), together with elemental components obtained with the scanning electron microscope.

Polished sections of mahlmoodite spherules were analyzed using an ARL-SEM-Q microprobe. (The core grains did not survive the polishing process.) The polished spherulite rims were analyzed using 15-kV accelerating voltage, 0.1-A beam current, and 20-s count times. The intensity data were corrected by the matrix correction procedures of Bence and Albee (1968). Standards used were Durango apatite for Ca, P; synthetic zircon for Zr, Si; Ilmen ilmenite for Fe, Ti, Mn; Kakami hornblende for Mg, Na, Al; synthetic fluorophlogopite for F. The average composition of the mahlmoodite grains is summarized in Table 3. The major-element cation ratios (Fe, P, Zr) are near to the ideal values for the formula $\text{FeZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. If minor-element values are com-

bined as substituents of major elements according to probable coordination (Ca, Mn, Mg, Al for Fe; Ti for Zr), the ratios are improved. The sum deficit presumably corresponds to H_2O in the amount of $3.2\text{H}_2\text{O}$; some (inter-layer) H_2O was probably lost in the vacuum.

Several attempts by John Marinenko (U.S. Geological Survey) to synthesize mahlmoodite by direct methods were unsuccessful. Alluli et al. (1976) synthesized their compounds by base exchange from acetate solutions of the cations into solid $\text{NaHZr}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$; such a procedure is so far the only known method of preparation. Probably mahlmoodite was formed directly from mineralizing solutions rather than by base exchange.

Although the mineral has not yet been synthesized in the laboratory, the extensive studies of Clearfield and Alluli and their colleagues have made it possible to confirm conclusively the chemical composition of mahlmoodite and to understand its structural properties. Starting with $\gamma\text{-Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, Clearfield and Kalnins (1978) prepared a series of compounds $\gamma\text{-MZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ with $\text{M} = \text{Mn, Ni, Co, Cu, and Zn}$; these compounds are evidently dimorphous with the series of Alluli et al. (1976), who derived theirs from $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$. Probably corresponding Fe dimorphs (including mahlmoodite) could exist when formed under appropriately reducing conditions. The structure studies of Clearfield and his colleagues have shown that all of these compounds are based on an orthogonal layer structure, in which the layer consists of a corner-shared linkage of PO_4 tetrahedra and ZrO_6 octahedra (Fig. 3). A review paper describing the general chemistry and properties of the zirconium phosphates, which have important applications as industrial ion exchange media, has been published by Alberti (1978).

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