

## THE CRYSTAL STRUCTURE OF MALHMOODITE FROM CUSTER, SOUTH DAKOTA, USA

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### ABSTRACT

An occurrence of malhmoodite,  $\text{Fe}^{2+}\text{Zr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , from the Scott's Rose Quartz mine, Custer County, South Dakota, USA, has been identified. It occurs as divergent groups of yellowish, flat-lying platy crystals on football-size masses of altered löllingite with scorodite, parasymplectite, karibibite, schneiderhöhnite, kahlerite, and zircon. An electron probe microanalysis of malhmoodite yielded an empirical formula (based on 12 O *apfu*) of  $\text{Fe}_{1.06}(\text{Zr}_{1.10}\text{Hf}_{0.03})_{\Sigma 1.13}[(\text{P}_{0.93}\text{As}_{0.01})_{\Sigma 0.94}\text{O}_4]_2 \cdot 4\text{H}_2\text{O}$ .

Single-crystal X-ray structure analysis shows that malhmoodite is the Fe-analogue of zigrasite,  $\text{MgZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ . Malhmoodite is triclinic with space group  $P\bar{1}$  and unit-cell parameters  $a = 5.31200(10)$ ,  $b = 9.3419(3)$ ,  $c = 9.7062(3)$  Å,  $\alpha = 97.6111(13)$ ,  $\beta = 91.9796(11)$ ,  $\gamma = 90.3628(12)^\circ$ ,  $V = 477.10(2)$  Å<sup>3</sup>,  $Z = 2$ , in contrast to the previously reported monoclinic symmetry with space group  $P2_1/c$  and unit-cell parameters  $a = 9.12(2)$ ,  $b = 5.42(1)$ ,  $c = 19.17(2)$  Å,  $\beta = 94.8(1)^\circ$ ,  $V = 944.26$  Å<sup>3</sup>,  $Z = 4$ . The crystal structure of malhmoodite is characterized by sheets composed of  $\text{ZrO}_6$  octahedra sharing all vertices with  $\text{PO}_4$  tetrahedra. These sheets are parallel to (001) and are joined together by the  $\text{FeO}_2(\text{H}_2\text{O})_4$  octahedra. The structure determination of malhmoodite, along with that of zigrasite, warrants a re-investigation of synthetic compounds  $M^{2+}\text{Zr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  ( $M = \text{Mn}, \text{Ni}, \text{Co}, \text{Cu}, \text{or Zn}$ ) that have been assumed previously to be monoclinic.

**Keywords:** malhmoodite, phosphate, crystal structure, zigrasite, Black Hills.

### INTRODUCTION

Malhmoodite,  $\text{Fe}^{2+}\text{Zr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , is a rare phosphate mineral. It was first noted and correctly formulated by Hey *et al.* (1982) from white spherules (<0.5 mm in diameter) perched on radial groups of kolbeckite plates and black pyroxene crystals collected from the Union Carbide Vanadium mine at Wilson Springs, Garland County, Arkansas, USA. The formal description of malhmoodite as a new mineral species was presented by Milton *et al.* (1993). By means of energy dispersive X-ray analysis and powder X-ray

diffraction, Elton & Hooper (1995) confirmed a second occurrence of malhmoodite from Kerriack Cove, Cornwall, England. Malhmoodite from both Wilson Springs, Arkansas, and Kerriack Cove, England, occurs as tiny compact spherules of radiating acicular or lath-like crystals. However, due to the small size of individual crystals (< 0.050 × 0.005 × 0.001 mm), the crystal structure of malhmoodite remained undetermined until now. This study reports a new occurrence of malhmoodite from the Scott's Rose Quartz mine, Custer County, South Dakota, USA, and its crystal structure determination, demonstrating that the previ-

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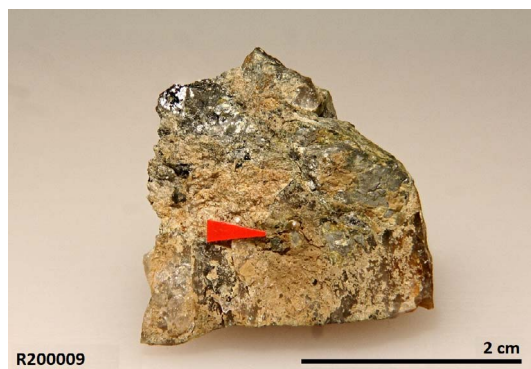


FIG. 1. The specimen on which yellowish, flat-lying plates, divergent groups of malhmoodite crystals, were found on a matrix of altered löllingite with scorodite and parasymplectite, and to a lesser degree karibibite, schneiderhöhnite, kahlerite, and 1–3 mm zircons.

ously determined monoclinic symmetry from the powder X-ray diffraction data is incorrect and the real symmetry of malhmoodite is triclinic, isostructural with zigrasite,  $\text{MgZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  (Hawthorne *et al.* 2009, Hawthorne & Simmons 2010).

#### OCCURRENCE

The malhmoodite sample used for this study was collected from the Scott's Rose Quartz mine, which has been in intermittent operation since 1893 and is located about 11 km southeast of Custer in the southern Black Hills of South Dakota. The mine is a classic fractionated pegmatite related to the 1.7 b.y. Harney Peak granite (Redden *et al.* 1982, Redden & DeWitt 2008). Malhmoodite occurs as yellowish flat-lying plates, divergent groups on a matrix (Figs. 1, 2) of football-size masses of altered löllingite with



FIG. 2. A microscopic view of yellowish, flat-lying plates, divergent groups of malhmoodite crystals.

TABLE 1. POWDER X-RAY DIFFRACTION DATA FOR MALHMOODITE

$I\%$	$d_{\text{meas}}$	$d_{\text{cal}}$	$hkl$	$I\%$	$d_{\text{meas}}$	$d_{\text{cal}}$	$hkl$
27	9.678	9.618	0 0 1	4	1.836	1.838	1 1 $\bar{5}$
18	4.792	4.809	0 0 2	12	1.786	1.790	0 4 $\bar{4}$
63	4.579	4.584	1 1 0	6	1.752	1.750	2 $\bar{4}$ 1
63	4.405	4.407	0 2 $\bar{1}$	16	1.707	1.705	2 4 1
9	4.239	4.226	1 $\bar{1}$ 1	7	1.666	1.673	2 4 1
100	4.109	4.119	1 $\bar{1}$ 1	10	1.640	1.641	2 2 4
28	3.983	3.991	1 1 1	5	1.583	1.586	2 0 $\bar{5}$
23	3.576	3.580	0 2 $\bar{2}$	6	1.559	1.558	0 6 $\bar{1}$
5	3.474	3.491	1 1 $\bar{2}$	8	1.526	1.528	3 3 0
19	3.270	3.282	1 1 2	4	1.496	1.499	3 3 $\bar{2}$
35	3.165	3.169	1 1 2	8	1.466	1.470	1 3 5
23	2.811	2.815	0 2 3	2	1.435	1.438	1 3 6
80	2.662	2.684	1 $\bar{3}$ 0	1	1.413	1.417	3 3 2
15	2.588	2.596	1 1 3	3	1.404	1.403	3 $\bar{1}$ 4
4	2.509	2.504	2 1 1	4	1.368	1.367	0 2 7
13	2.472	2.489	0 2 3	7	1.341	1.342	2 $\bar{6}$ 0
3	2.299	2.292	2 2 0	10	1.324	1.327	4 0 0
8	2.246	2.255	1 3 2	2	1.303	1.306	1 1 7
9	2.205	2.204	0 4 $\bar{2}$	4	1.286	1.289	1 7 0
4	2.152	2.151	2 2 $\bar{2}$	1	1.265	1.264	3 5 2
3	2.114	2.113	2 2 2	2	1.244	1.245	0 4 6
4	2.083	2.083	2 0 $\bar{3}$	1	1.232	1.233	3 5 $\bar{3}$
11	2.057	2.059	2 2 2	3	1.184	1.185	3 3 5
19	1.996	1.995	2 2 2	3	1.160	1.164	3 3 $\bar{6}$
4	1.923	1.926	1 3 3	4	1.136	1.134	0 6 5
3	1.876	1.882	1 3 4				

scorodite and parasymplectite, and to a lesser degree karibibite, schneiderhöhnite, kahlerite, and 1–3 mm zircons. Malhmoodite was likely formed by residual fluids carrying zirconium and phosphate. Although phosphate minerals are uncommon in the Scott's Rose Quartz mine, metasomatic fluids supplied during end-stage solidification of the pegmatite may have played a role with minor leached phosphate from amblygonite and triphylite, both of which occur in the mine. Rounded crystals of zircon probably supplied additional zirconium. The löllingite was found in the mine dumps with microcline. The malhmoodite sample is now in the collection of the RRUFF Project with the deposition number R200009 (<http://rruff.info/R200009>).

#### CHEMICAL COMPOSITION AND RAMAN SPECTRUM

The chemical composition of malhmoodite was measured using a Shimadzu EPMA-1720 with an accelerating voltage of 15 kV, beam current 10 nA, and beam size 1  $\mu\text{m}$ . The standards included  $\text{ZrSiO}_4$  (Zr),  $\text{HfSiO}_4$  (Hf),  $\text{Fe}_3\text{O}_4$  (Fe),  $\text{FeAsS}$  (As), and  $\text{InP}$  (P), yielding an average composition (wt.%) (eight

TABLE 2. COMPARISON OF MINERALOGICAL DATA FOR MALHMOODITE AND ZIGRASITE

	Malhmooodite	Malhmooodite	Zigrasite
Ideal chemical formula	Fe <sup>2+</sup> Zr(PO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	Fe <sup>2+</sup> Zr(PO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	MgZr(PO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O
Crystal symmetry	Triclinic	Monoclinic (assumed)	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i> (assumed)	<i>P</i> $\bar{1}$
<i>a</i> (Å)	5.31200(10)	9.12(2)	5.3049(2)
<i>b</i> (Å)	9.3419(3)	5.42(1)	9.3372(4)
<i>c</i> (Å)	9.7062(3)	19.17(2)	9.6282(5)
$\alpha$ (°)	97.6111(13)	90	97.348(1)
$\beta$ (°)	91.9796(11)	94.8(1)	91.534(1)
$\gamma$ (°)	90.3628(12)	90	90.512(4)
<i>V</i> (Å <sup>3</sup> )	477.10(2)	944.26	472.79(5)
<i>Z</i>	2	4	2
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	2.878	2.877	2.66
No. of reflections collected	12,014		14,396
No. of independent reflections	2806		2766
No. of reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	2174		2623
No. of parameters refined	161		
R(int)	0.028		0.016
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> factors [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.032, 0.079		0.0375, 0.0872
Goodness-of-fit	1.055		
Crystal locality	Scott's Rose Quartz mine, Custer County, SD, USA	Union Carbide mine, Garland County, AR, USA	Dunton Quarry, Oxford County, ME, USA
Reference	(1)	(2)	(3)

Note: (1) This study; (2) Milton *et al.* (1993); (3) Hawthorne & Simmons (2010).

points) of ZrO<sub>2</sub> 28.12(58), HfO<sub>2</sub> 2.35(34), FeO 17.45(39), P<sub>2</sub>O<sub>5</sub> 33.66(36), and As<sub>2</sub>O<sub>5</sub> 0.94(28). The H<sub>2</sub>O content (17.36 wt.%) was added to achieve the ideal 4H<sub>2</sub>O value, bringing the total to 99.88(57) wt.%. The resultant empirical formula, calculated on the basis of 12 O *apfu* (from the structure determination) is Fe<sub>1.01</sub>(Zr<sub>0.95</sub>Hf<sub>0.05</sub>) $\Sigma_{1.00}$ [(P<sub>0.98</sub>As<sub>0.02</sub>) $\Sigma_{1.00}$ O<sub>4</sub>]<sub>2</sub>·4H<sub>2</sub>O, ideally FeZr(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O.

The Raman spectrum of malhmooodite was collected from a randomly oriented crystal with a Thermo Alpha microRaman system, using a solid-state laser with a frequency of 532 nm at the full power of 150 mW and a thermoelectrically cooled CCD detector. The laser is partially polarized with 4 cm<sup>-1</sup> resolution and a spot size of 1  $\mu$ m.

#### X-RAY CRYSTALLOGRAPHY AND STRUCTURE DETERMINATION

Powder X-ray diffraction data for malhmooodite (Table 1) were collected with a Rigaku Synergy diffractometer in the Gandolfi mode with Cu-radiation at 50 kV and 1 mA. The unit-cell parameters refined from these data are *a* = 5.3070(2), *b* = 9.3431(3), *c* = 9.6949(3) Å,  $\alpha$  = 97.473(3),  $\beta$  = 91.985(3),  $\gamma$  = 90.460(3)°, *V* = 476.30 (2) Å<sup>3</sup>.

Single-crystal X-ray diffraction data for malhmooodite were collected using a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-mono-chromatized MoK $\alpha$  radiation, with frame widths of 0.5° in  $\omega$  and 30 s counting time per frame. All reflections were indexed on the basis of a triclinic unit cell (Table 2). The intensity data were corrected for X-ray absorption using the Bruker program SADABS. The systematic absences of reflections suggest the possible space group *P*1 or *P* $\bar{1}$ . The crystal structure was solved and refined using SHELX-2018 (Sheldrick 2015a, b) based on the space group *P* $\bar{1}$  because it yielded better refinement statistics in terms of bond lengths and angles, atomic displacement parameters, and *R* factors. All H atoms were located from the difference-Fourier synthesis. The positions of all atoms were refined with anisotropic displacement parameters, except for H atoms, which were refined with *U*<sub>iso</sub> values 1.5 times those of the O atoms on which they ride. During the refinements, all atomic sites were assumed to be fully occupied and a small amount of Hf detected from the electron probe microanalysis was assigned to the Zr site. The refined Zr/Hf ratio (0.932/0.068) is very close to that (0.95/0.05) determined from the electron probe microanalysis. Nonetheless, we fixed the Zr/Hf ratio to that

TABLE 3. FRACTIONAL ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ ) FOR MALHMOODITE

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zr	0.25126 (5)	0.74833 (3)	0.49328 (3)	0.00673 (10)
Fe1	0	0	0	0.01812 (16)
Fe2	1/2	1/2	0	0.01849 (16)
P1	0.26803 (13)	0.44975 (8)	0.67923 (7)	0.00733 (16)
P2	0.23105 (13)	0.05873 (8)	0.32392 (7)	0.00716 (16)
O1	0.3138 (4)	0.5927 (2)	0.6219 (2)	0.0172 (5)
O2	0.2400 (4)	0.4793 (3)	0.8358 (2)	0.0165 (5)
O3	0.4908 (4)	0.3487 (2)	0.6453 (2)	0.0144 (4)
O4	0.0276 (4)	0.3771 (3)	0.6132 (2)	0.0171 (5)
O5	0.0045 (4)	0.1532 (3)	0.3678 (2)	0.0171 (5)
O6	0.2544 (4)	0.0511 (3)	0.1667 (2)	0.0166 (5)
O7	0.4707 (4)	0.1258 (2)	0.3971 (2)	0.0150 (5)
O8	0.1891 (4)	-0.0940 (2)	0.3622 (2)	0.0158 (5)
O9	0.2822 (5)	0.8620 (3)	0.8958 (2)	0.0228 (5)
H1	0.442182	0.907426	0.883049	0.034*
H2	0.218122	0.811496	0.804750	0.034*
O10	0.1669 (5)	0.1597 (3)	0.8870 (3)	0.0306 (6)
H3	0.112438	0.262558	0.931239	0.046*
H4	0.146870	0.142403	0.789609	0.046*
O11	0.2224 (5)	0.3866 (3)	0.1139 (3)	0.0270 (6)
H5	0.080462	0.452689	0.130208	0.041*
H6	0.267738	0.359373	0.204668	0.041*
O12	0.3139 (5)	0.6857 (3)	0.0892 (3)	0.0300 (6)
H7	0.301599	0.765506	0.024556	0.045*
H8	0.332615	0.728364	0.189215	0.045*

Note: (1) \* refers to  $U_{\text{iso}}$ . (2) The site occupancy for the Zr site is (0.95Zr + 0.05Hf).

determined from the microanalysis to avoid inconsistency in the structural refinements. The final coordinates and displacement parameters of atoms are given in Table 3 and selected bond distances in Table 4.

## RESULTS AND DISCUSSION

Milton *et al.* (1993) measured the powder X-ray diffraction data of malhmoodite with a Gandolfi camera. By assuming that it was analogous to a series of synthetic compounds of the type  $MZr(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  (Allulli *et al.* 1976), where  $M$  is a divalent cation Mn, Ni, Co, Cu, or Zn, they indexed their powder X-ray diffraction data (15 sharp lines) based on monoclinic symmetry in space group  $P2_1/c$  and obtained the unit-cell dimensions:  $a = 9.12(2)$ ,  $b = 5.42(1)$ ,  $c = 19.17(2)$  Å,  $\beta = 94.8(1)^\circ$ , and  $Z = 4$ .

Figure 3 is a comparison of the powder X-ray diffraction data of malhmoodite from this study with those from Milton *et al.* (1993). The marked resemblance between the two is obvious. However, our single-crystal X-ray diffraction data reveal that the real symmetry of malhmoodite is triclinic with space group  $P\bar{1}$ , in contrast to that reported by Milton *et al.*

(1993). Table 2 lists the unit-cell parameters from this study and those determined by Milton *et al.* (1993). As demonstrated by Hawthorne & Simmons (2010), the monoclinic unit cell of Milton *et al.* (1993), which can be obtained by two triclinic cells that are related by the transformation matrix (0 1 0 / 1 0 0 / 0 0 2), is only pseudometrically monoclinic.

The single-crystal X-ray structure determination shows that malhmoodite is the Fe-analogue of zigrasite,  $\text{MgZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  (Hawthorne & Simmons 2010). Its crystal structure contains two symmetrically independent  $\text{PO}_4$  tetrahedra, one  $\text{ZrO}_6$  octahedra, and two  $\text{FeO}_2(\text{H}_2\text{O})_4$  octahedra. The  $\text{ZrO}_6$  octahedra share all vertices with the  $\text{PO}_4$  tetrahedra to form sheets parallel to (001) (Fig. 4), which are joined together by the  $\text{FeO}_2(\text{H}_2\text{O})_4$  octahedra along  $c$  (Fig. 5). Topologically, the  $[\text{Zr}(\text{PO}_4)_2]$ -type sheets in malhmoodite are identical to those in merwinite,  $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$  (Moore & Araki 1972); wycheproofite,  $\text{NaAlZr}(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$  (Kolitsch 2003); and apthitalite,  $\text{K}_3\text{Na}(\text{SO}_4)_2$  (Okada & Ossaka 1980), as noted by Hawthorne & Simmons (2010). Interestingly, Fleck *et al.* (2002) considered such sheets to consist of kröhnkite-type chains linked together by sharing polyhedral vertices.

TABLE 4. ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ ) FOR MALHMOODITE

Atom	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zr	0.00608 (13)	0.00555 (14)	0.00850 (14)	0.00018 (8)	-0.00084 (8)	0.00098 (9)
Fe1	0.0143 (3)	0.0281 (4)	0.0122 (3)	-0.0021 (3)	-0.0020 (2)	0.0041 (3)
Fe2	0.0182 (3)	0.0234 (4)	0.0132 (3)	0.0022 (3)	-0.0026 (2)	0.0007 (3)
P1	0.0071 (3)	0.0070 (4)	0.0078 (3)	0.0002 (3)	-0.0008 (3)	0.0008 (3)
P2	0.0071 (3)	0.0065 (4)	0.0078 (3)	0.0002 (3)	-0.0004 (3)	0.0010 (3)
O1	0.0212 (12)	0.0116 (11)	0.0207 (11)	-0.0008 (9)	-0.0007 (9)	0.0096 (9)
O2	0.0168 (11)	0.0233 (13)	0.0092 (10)	0.0027 (9)	0.0005 (8)	0.0017 (9)
O3	0.0142 (10)	0.0152 (11)	0.0139 (10)	0.0062 (9)	0.0017 (8)	0.0012 (8)
O4	0.0115 (11)	0.0172 (12)	0.0208 (11)	-0.0058 (9)	-0.0050 (8)	-0.0023 (9)
O5	0.0136 (11)	0.0171 (12)	0.0195 (11)	0.0048 (9)	0.0031 (8)	-0.0028 (9)
O6	0.0133 (11)	0.0268 (13)	0.0098 (10)	-0.0026 (9)	-0.0010 (8)	0.0035 (9)
O7	0.0140 (11)	0.0151 (11)	0.0150 (10)	-0.0047 (8)	-0.0052 (8)	0.0004 (9)
O8	0.0193 (11)	0.0104 (11)	0.0186 (11)	-0.0032 (9)	-0.0050 (9)	0.0067 (9)
O9	0.0172 (12)	0.0330 (15)	0.0180 (12)	-0.0031 (10)	0.0023 (9)	0.0027 (11)
O10	0.0307 (15)	0.0285 (15)	0.0331 (15)	-0.0054 (12)	-0.0004 (12)	0.0063 (12)
O11	0.0222 (13)	0.0302 (15)	0.0297 (14)	0.0025 (11)	0.0085 (11)	0.0058 (12)
O12	0.0359 (15)	0.0299 (16)	0.0241 (13)	0.0124 (12)	-0.0003 (11)	0.0034 (12)

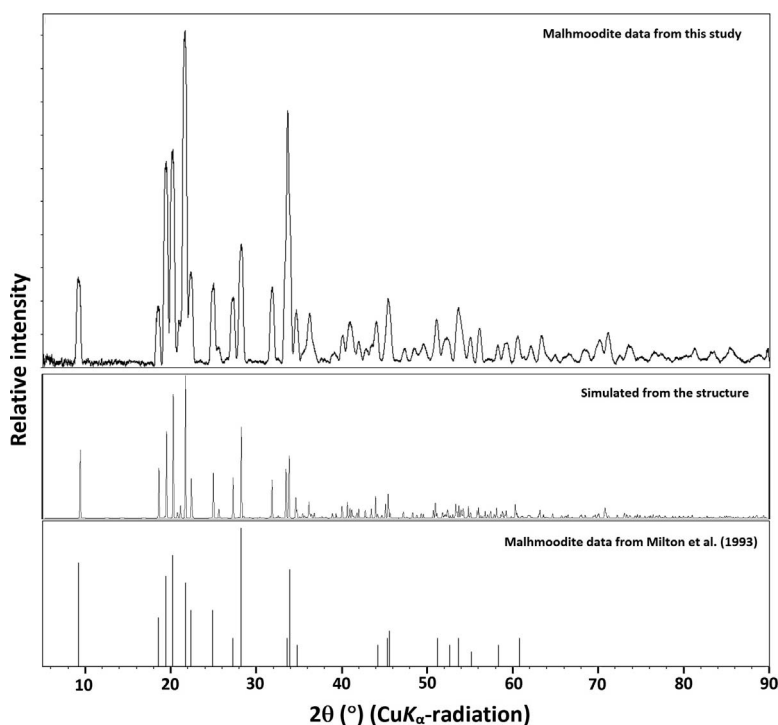


Fig. 3. Comparison of powder X-ray diffraction data for malhmoodite. The data for malhmoodite from the type locality (Wilson Springs, Arkansas) were taken from Milton *et al.* (1993).

All structural features of malhmoodite are similar to those of zigrasite, including the  $\text{PO}_4$  and  $\text{ZrO}_6$  polyhedral geometries and hydrogen bonding schemes (Hawthorne & Simmons 2010). The major difference

between the two structures is that both  $\text{FeO}_2(\text{H}_2\text{O})_4$  octahedra in malhmoodite appear, unsurprisingly, to be slightly larger than the corresponding  $\text{MgO}_2(\text{H}_2\text{O})_4$  octahedra in zigrasite, as indicated by the average



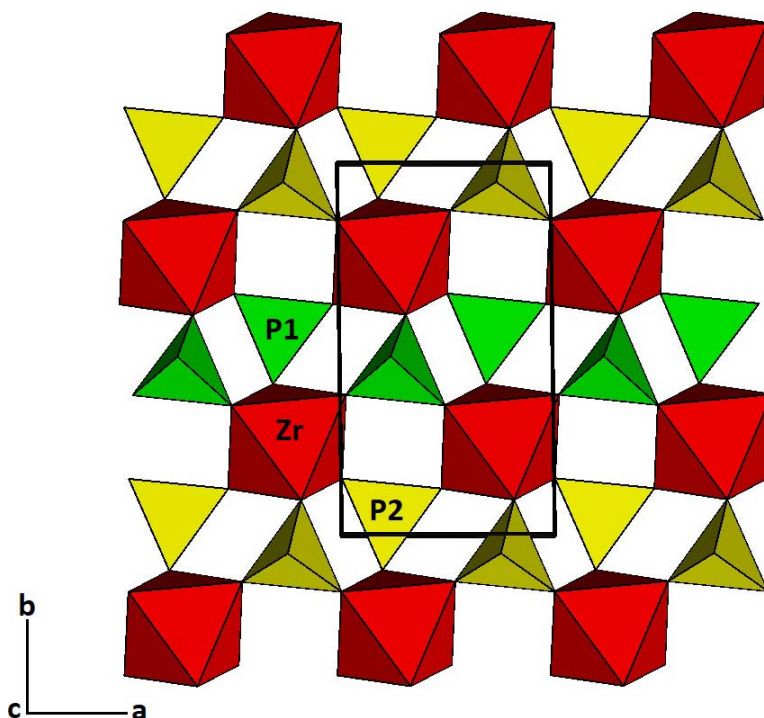


FIG. 4. Crystal structure of malhmoodite, showing a sheet composed of  $ZrO_6$  octahedra sharing all vertices with  $PO_4$  tetrahedra.

bond distances of  $\langle Fe1-O \rangle = 2.138 \text{ \AA}$  and  $\langle Fe2-O \rangle = 2.127 \text{ \AA}$  versus  $\langle Mg1-O \rangle = 2.075 \text{ \AA}$  and  $\langle Mg2-O \rangle = 2.065 \text{ \AA}$  (Table 5).

The Raman spectrum of malhmoodite between 100 and  $4000 \text{ cm}^{-1}$  is displayed in Figure 6. Based on previous Raman spectroscopic studies of various hydrous phosphate minerals (*e.g.*, Litasov & Podgornykh 2017, Ogorodova *et al.* 2020 and references therein), we made the following tentative assignments for the major Raman

bands. The bands between  $3300$  and  $3650 \text{ cm}^{-1}$  originate from O–H stretching vibrations and those between  $1480$  and  $1680 \text{ cm}^{-1}$  from H–O–H bending vibrations. The bands from  $900$  to  $1200 \text{ cm}^{-1}$  are ascribable to P–O stretching vibrations within the  $PO_4$  group, whereas those from  $400$  to  $660 \text{ cm}^{-1}$  are due to O–P–O bending vibrations. The bands below  $400 \text{ cm}^{-1}$  are mainly associated with the rotational and translational modes of the  $PO_4$  tetrahedra, as well as the  $M-O$  ( $M = Fe$  and  $Zr$ ) interactions and lattice vibrational modes. For comparison, the Raman spectra of malhmoodite from the type locality (Wilson Springs, Arkansas) and isostructural zigrasite, both being in the collection of the RRUFF Project (<http://rruff.info/R060462> and <https://rruff.info/R120143>, respectively) were included in Figure 6. The resemblances among the three spectra are evident. The difference in peak intensities for the three spectra principally results from the different crystal orientations when the data were collected.

Zirconium phosphate materials with layered structures have been investigated extensively because of their great potential as ion-exchangers, intercalating supporters, and microwave absorbers (*e.g.*, Alberti 1978, Szirtes *et al.* 2001, Ferragina *et al.* 2005, Hu *et al.* 2020). In particular, a series of compounds with the general formula  $M^{2+}Zr(PO_4)_2 \cdot 4H_2O$  ( $M = Mn, Ni, Co, Cu, \text{ or } Zn$ ) have been synthesized (Allulli *et al.* 1976, Hu *et al.* 2020). The

TABLE 5. SELECTED BOND DISTANCES ( $\text{\AA}$ ) FOR MALHMOODITE

P1–O1	1.534(2)	P2–O5	1.535(2)
–O2	1.521(2)	–O6	1.538(2)
–O3	1.536(2)	–O7	1.526(2)
–O4	1.523(2)	–O8	1.539(2)
$\langle P1-O \rangle$	1.529	$\langle P2-O \rangle$	1.532
Zr–O1	2.060(2)	Fe1–O6	2.076(2) $\times 2$
–O3	2.080(2)	–O9	2.172(3) $\times 2$
–O4	2.046(2)	–O10	2.168(3) $\times 2$
–O5	2.080(2)	$\langle Fe1-O \rangle$	2.138
–O7	2.058(2)	Fe2–O2	2.061(2) $\times 2$
–O8	2.090(2)	–O11	2.219(3) $\times 2$
$\langle Zr-O \rangle$	2.069	–O12	2.102(3) $\times 2$
		$\langle Fe2-O \rangle$	2.127

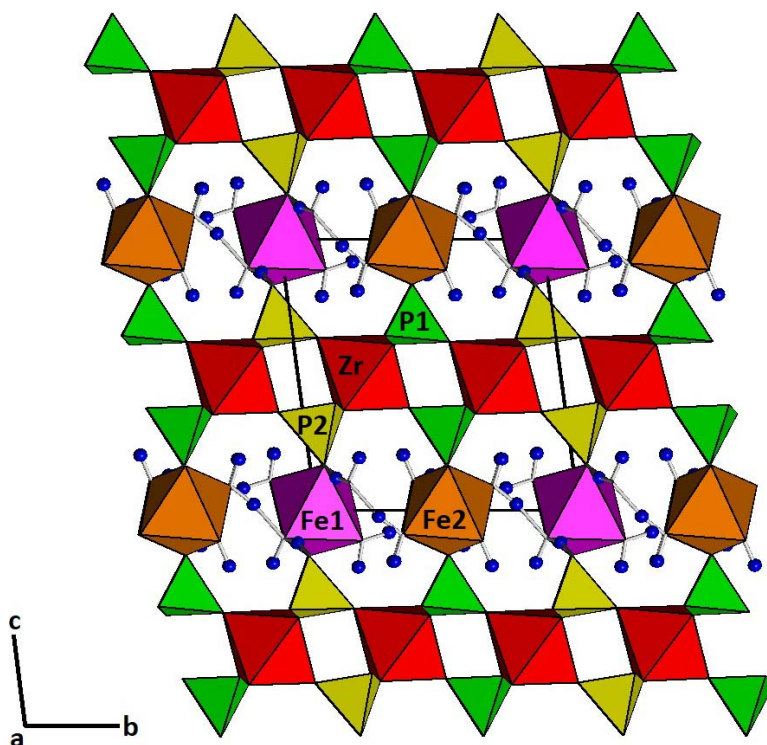


FIG. 5. The crystal structure of malhmoodite, showing the  $[\text{Zr}(\text{PO}_4)_2]$  sheets linked by  $\text{FeO}_2(\text{H}_2\text{O})_4$  octahedra. Small blue spheres represent H atoms.

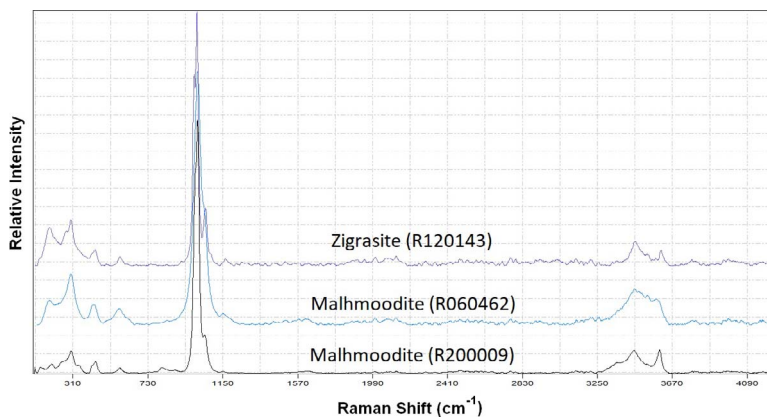


FIG. 6. Raman spectra of malhmoodite, along with that of zigrasite for comparison.

powder X-ray diffraction data of these materials are remarkably similar to those of malhmoodite, with a characteristic peak at  $\sim 9.6 \text{ \AA}$  that is indicative of the interlayer distance (Allulli *et al.* 1976, Milton *et al.* 1993, Hu *et al.* 2020). Nonetheless, all these compounds have previously been assumed to be monoclinic and the peak at

$\sim 9.6 \text{ \AA}$  indexed as  $d_{002}$ . With the structure determinations for zigrasite ( $M = \text{Mg}$ ) (Hawthorne & Simmons 2010) and malhmoodite ( $M = \text{Fe}$ ) (this study), it appears to be necessary to re-examine the crystal symmetry for the materials with  $M = \text{Mn}, \text{Ni}, \text{Co}, \text{Cu},$  or  $\text{Zn}$ .

Interestingly, using  $\gamma$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O as the starting material, which was different from that [ $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O] used by Allulli *et al.* (1976), Clearfield & Kalnins (1978) also prepared a series of compounds  $M^{2+}$ Zr(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O with  $M$  = Mn, Ni, Co, Cu, or Zn. However, their powder X-ray diffraction data for these compounds all exhibit a characteristic peak at ~12 Å, apparently different from those obtained by Allulli *et al.* (1976), indicating that the  $M^{2+}$ Zr(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O-type compounds possess dimorphs. Perhaps the dimorphs of FeZr(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (malhmoodite) and/or MgZr(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (zigrasite) could also be synthesized or found in nature.

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