# Ophirite, Ca<sub>2</sub>Mg<sub>4</sub>[Zn<sub>2</sub>Mn<sup>3+</sup><sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(Fe<sup>3+</sup>W<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]·46H<sub>2</sub>O, a new mineral with a heteropolytungstate tri-lacunary Keggin anion

## ANTHONY R. KAMPF<sup>1</sup>, JOHN M. HUGHES<sup>2,\*</sup>, BARBARA P. NASH<sup>3</sup>, STEPHEN E. WRIGHT<sup>4</sup>, GEORGE R. ROSSMAN<sup>5</sup> AND JOE MARTY<sup>6</sup>

<sup>1</sup>Mineral Sciences Department, Natural History Museum of Los Angeles County, Los Angeles, California 90007, U.S.A.
 <sup>2</sup>Department of Geology, University of Vermont, Burlington, Vermont 05405, U.S.A.
 <sup>3</sup>Department of Geology and Geophysics, University of Utah, Salt Lake City, Utah 84112, U.S.A.

pariment of Geology and Geophysics, University of Utan, Sait Lake City, Utan 84112, U.S.A

<sup>4</sup>Department of Statistics, Miami University, Oxford, Ohio 45056, U.S.A.

<sup>5</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, U.S.A. <sup>6</sup>5199 E. Silver Oak Road, Salt Lake City, Utah 84108, U.S.A.

## ABSTRACT

Ophirite, Ca<sub>2</sub>Mg<sub>4</sub>[Zn<sub>2</sub>Mn<sub>2</sub><sup>3+</sup>(H<sub>2</sub>O)<sub>2</sub>(Fe<sup>3+</sup>W<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]·46H<sub>2</sub>O, is a new mineral species from the Ophir Hill Consolidated mine, Ophir district, Oquirrh Mountains, Tooele County, Utah, U.S.A. Crystals of ophirite are orange-brown tablets on {001} with irregular {100} and {110} bounding forms; individual crystals are up to about 1 mm in maximum dimension and possess a pale orange streak. The mineral is transparent, with a vitreous luster; it does not fluoresce in short- or long-wave ultraviolet radiation. Ophirite has a Mohs hardness of approximately 2 and brittle tenacity. No cleavage or parting was observed in the mineral. The fracture is irregular. The density calculated from the empirical formula using the single-crystal cell data is 4.060 g/cm<sup>3</sup>. Ophirite is biaxial (+) with a 2*V* angle of 43(2)°. Indices of refraction for ophirite are  $\alpha = 1.730(3)$ ,  $\beta = 1.735(3)$ ,  $\gamma = 1.770(3)°$ . The optic orientation (incompletely determined) is  $Y \angle \mathbf{b}$  $\approx 9°$  and one optic axis is approximately perpendicular to {001}. Dispersion r > v, strong; pleochroism is *X* = light orange brown, *Y* = light orange brown, *Z* = orange brown; *X* < *Y* << *Z*. Chemical analyses of ophirite were obtained by electron probe microanalysis; optimization of that analysis using the results of the crystal-structure analysis yielded the formula

 $\begin{array}{l} (Ca_{1.46}Mg_{0.50}Zn_{0.04})_{\Sigma 2.00}(Mg_{3.96}Mn_{0.04}^{3+})_{\Sigma 4.00}[(Zn_{1.16}Fe_{0.68}^{3+}Ca_{0.14}Sb_{0.02}^{5+})_{\Sigma 2.00}(Mn_{1.42}^{3+}Sb_{0.32}^{5+}Fe_{0.24}^{3+}W_{0.02})_{\Sigma 2.00}\\ \{(H_2O)_2[(Fe_{0.80}^{3+}Sb_{0.11}^{5+}Ca_{0.07}Mg_{0.02})_{\Sigma 1.00}(W_{8.71}Mn_{0.29}^{3+})_{\Sigma 1.00}]_2\}]\cdot 46H_2O; \end{array}$ 

the simplified formula of ophirite is  $Ca_2Mg_4[Zn_2Mn_2^{3+}(H_2O)_2(Fe^{3+}W_9O_{34})_2] \cdot 46H_2O$ . Ophirite is triclinic,  $P\overline{1}$ , with a = 11.9860(2), b = 13.2073(2), c = 17.689(1) Å,  $\alpha = 69.690(5)$ ,  $\beta = 85.364(6)$ ,  $\gamma = 64.875(5)^{\circ}$ , V = 2370.35(18) Å<sup>3</sup>, and Z = 1. The strongest four lines in the diffraction pattern are [d in Å (I)(hkl)]:  $10.169(100)(100,110), 11.33(91)(011,010), 2.992(75)(334,341,\overline{115}), and 2.760(55)(412,006,\overline{135}).$  The atomic arrangement of ophirite was solved and refined to  $R_1 = 0.0298$  for 9230 independent reflections. The structural unit, ideally  $\{ {}^{[6]}Zn_2 {}^{[6]}Mn_2^{3+}(H_2O)_2({}^{[4]}Fe^{3+[6]}W_9^{6+}O_{34})_2 \} {}^{12-}$ , consists of a  $[Zn_2Mn_2^{3+}(H_2O)_2]$  octahedral layer sandwiched between opposing heteropolytungstate tri-lacunary (<sup>[4]</sup>Fe<sup>3+[6]</sup>W<sub>9</sub><sup>(-1</sup>O<sub>34</sub>) Keggin anions. Similar structures with an octahedral layer between two tri-lacunary Keggin anions are known in synthetic phases. Charge balance in the ophirite structure is maintained by the  $\{[Mg(H_2O)_6]_4[Ca$ (H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>·10H<sub>2</sub>O}<sup>12+</sup> interstitial unit. The interstitial unit in the structure of ophirite is formed of two distinct Mg(H<sub>2</sub>O)<sub>6</sub> octahedra and a Ca(H<sub>2</sub>O)<sub>6</sub>O<sub>1</sub> polyhedron, as well as five isolated water molecules. The linkage between the structural unit and the interstitial unit results principally from hydrogen bonding between oxygen atoms of the structural unit with hydrogen atoms of the interstitial unit. Ophirite is the first known mineral to contain a lacunary defect derivative of the Keggin anion, a heteropolyanion that is well known in synthetic phases. The new mineral is named ophirite to recognize its discovery at the Ophir Hill Consolidated mine, Ophir District, Oquirrh Mountains, Tooele County, Utah, U.S.A.

Keywords: Ophirite; new mineral species; heteropolytungstate lacunary Keggin anion; crystal structure; Ophir Hill Consolidated mine, Tooele County, Utah

## INTRODUCTION

The Ophir mining district, Utah, was organized shortly after ore deposits were discovered in the Oquirrh Mountains in 1865. For a century, the district was an important source of lead, zinc, copper, and silver ores until the close of the Ophir Hill Consolidated mine in 1972 (Marty and Wise 2008). The geologic setting of the Ophir district is given by those authors, and this brief summary is taken from their work. The Oquirrh Mountains are formed of allochthonous folded and faulted Paleozoic sedimentary rocks; these nappes were transported eastward in the Sevier thrust belt. In the Ophir district, in the southern portion of the Oquirrh Mountains, the sedimentary rocks form an 8000 ft sequence that

<sup>\*</sup> E-mail: jmhughes@uvm.edu

spans the entire Paleozoic, including limestone and dolomite with minor shale and sandstone. Throughout the district there are small intrusions of quartz monzonite porphyry that are spatially related to the ore, and may also be genetically related. Mineralization in the district is confined to a northwest-trending belt less than one mile wide and three miles in length, coincident with the crest of a broad, northwest plunging anticline. The Ophir district had a total production of 2.8 million tons of ore, averaging 6.5% Pb, 1.6% Zn, 0.8% Cu, 7.2 oz per ton Ag, and 0.006 oz per ton Au.

Herein, we describe a new mineral from the Ophir district. The new mineral species was discovered at the Ophir Hill Consolidated mine and is named ophirite in recognition of the type locality. The new mineral and name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2013-017). The two co-type specimens used in the description of the mineral are housed in the mineral collection of the Natural History Museum of Los Angeles County under catalog numbers 64029 and 64030. Ophirite is the first known mineral to contain a lacunary defect derivative of the Keggin anion, a heteropolyanion that is well known in synthetic phases, and its description introduces that polyanion and its associated structural groups to the mineralogical literature.

## **OCCURRENCE**

Ophirite was found underground at the Ophir Hill Consolidated mine, near a calcite cave known for the presence of micro-scheelite crystals. Unlike other mines in the district, the Ophir Hill Consolidated mine is dominated by sulfide minerals; this contrasts, for example, with the abundance of oxide minerals at the Hidden Treasure mine.

Tiny veinlets or stringers of black crystalline scheelite were found in the hanging wall adjacent to the cave. The only source of ophirite was a 6 cm wide and 1 m long veinlet, surrounded by a narrow zone of sericite-containing pyrite, with occasional foci of apatite, bournonite, galena, sphalerite, and other unidentified sulfides; rare crystals of fluorite and sulfur are also present in the veinlet. Among the black scheelite crystals are inclusions and pockets of dolomite. Ophirite crystals occur mostly at the interface between the dolomite and scheelite; it appears that late acidic and oxidizing hydrothermal solutions, in the presence of pyrite and calcium-rich hornfels, reacted with dolomite and scheelite to produce crystals of ophirite.

The compositions of veins in the mine vary considerably. The ore zones, which contain sulfides, were considerably larger and follow the limestone bedding planes. Other phases found in the mine include adularia, aurichalcite, azurite, boulangerite, bournonite, calcite, carbonatecyanotrichite, cerussite, chalcoalumite, chalcopyrite, cyanotrichite, dolomite, hübnerite, hydrozincite, ktenasite, linarite, malachite, marcasite, quartz, ralstonite, schulenbergite, serpierite, siderite, spangolite, tennantite, and tetrahedrite.

The clear evidence of oxidative alteration of the sulfides, most notably pyrite, is indicative of a late-stage mineral-forming environment that is relatively oxidized; however, the extent of the oxidation, and particularly the oxidation states of Fe and Mn (2+ or 3+), was not immediately evident. To determine oxidation states, we released the oxidation state in the optimization study and conducted optical spectroscopic studies, detailed below. The results, presented below, showed all cations to be in their fully oxidized states: Mg<sup>2+</sup>, Ca<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>3+</sup>, Sb<sup>5+</sup>, and W<sup>6+</sup>.

#### **PHYSICAL AND OPTICAL PROPERTIES**

Crystals of ophirite are tabular on {001} with irregular {100} and {110} bounding forms; individual crystals are up to about 1 mm in maximum dimension (Figs. 1 and 2). The vitreous and transparent crystals are orange-brown, with a pale orange streak. Ophirite is non-fluorescent in long- and short-wave ultraviolet light. It has a Mohs hardness of 2, brittle tenacity, irregular fracture, and no parting or cleavage. The density of ophirite could not be measured because there is insufficient material for direct measurement and the mineral slowly decomposes in Clerici solution; the calculated density is 4.060 g/cm<sup>3</sup> based on the empirical formula using single-crystal cell data.

The optical properties of ophirite were determined in white light. Ophirite is biaxial (+), with  $\alpha = 1.730(3)$ ,  $\beta = 1.735(3)$ ,  $\gamma = 1.770(3)^{\circ}$ . For ophirite,  $2V_{\text{meas}} = 43(2)^{\circ}$  by direct conoscopic measurement using a spindle stage, and  $2V_{\text{calc}} = 42.1^{\circ}$ . Dispersion is strong, r > v. Orientation (incompletely determined) is  $Y \angle \mathbf{b} \approx 9^{\circ}$ , with one optic axis approximately perpendicular to  $\{001\}$ . The pleochroism is X = light orange brown, Y = light orange brown, Z = orange brown; X < Y << Z.

## **Optical spectroscopy**

Optical spectra of ophirite (Fig. 3) were obtained on a 62  $\mu$ m diameter spot on an approximately 14.2  $\mu$ m thick, 176  $\times$ 



FIGURE 1. Crystals of ophirite from Ophir Hill Consolidated mine, Tooele County, Utah. Field of view is 1.4 mm.



**FIGURE 2.** Crystal drawing of ophirite (clinographic projection in standard orientation).

88 µm fragment with a prominent (001) face. Spectra were obtained with linearly polarized light oriented parallel to both extinction directions on this face. In this orientation, light was propagating close to one of the optic axes. A custom-built optical micro-spectrometer with a silicon diode-array detector was used.

The spectra in the two extinction directions are similar, showing an absorption tail rising toward the ultraviolet end of the spectrum with an obvious absorption band of moderate intensity superimposed at about 500 nm. Curve fitting indicates that the band is at about 490 nm. The spectra of Mn<sup>3+</sup> phases commonly occur in the 500 nm region, usually at a slightly longer wavelength, but sometimes at a slightly shorter wavelength.

To further test if this band could be from either  $Mn^{2+}$  or  $Mn^{3+}$ , the molar absorptivity ( $\varepsilon$ -value) was calculated from the average  $Mn_2O_3$  content (2.50 wt%), the absorbance determined from the curve fitting (about 0.1) and the density (4.06 g/cm<sup>3</sup>). A Beer's law calculation indicates that the  $\varepsilon$ -value is about 54, if all of the Mn contributes to this band. This is a value consistent with a spinallowed absorption from  $Mn^{3+}$ , but is inconsistent with the much less-intense spin-forbidden absorptions of  $Mn^{2+}$  that may have lower epsilons in this region (for example,  $\varepsilon$  for rhodochrosite is about 0.05 for the absorption bands between 450 and 550 nm). The only other cation likely to contribute to the optical absorption spectrum is iron, which is present at a concentration in the same range as manganese. Because the Fe<sup>2+</sup> spectrum is expected to occur at 800 nm or longer wavelengths, this oxidation state can be ruled out as the cause of the 500 nm absorption.

Like Mn<sup>2+</sup>, Fe<sup>3+</sup> also has spin-forbidden transitions, but when in a tetrahedral site will have greater intensity than when in the more common octahedral sites of low-absorption intensity. Two standards of Fe in tetrahedral oxygen coordination have been presented. In the spectrum of  $\gamma$ -LiAlO<sub>2</sub>:Fe<sup>3+</sup>, a band at 450 nm with  $\varepsilon = 17.2$  is prominent, along with significantly weaker features between 500 and 600 nm (Waychunas and Rossman 1983). In the spectrum of tetrahedral Fe<sup>3+</sup> in orthoclase (Faye 1969), a pair of bands occur at 417 and 441 nm with  $\varepsilon$  of about 1.5, with a much weaker band at 483 nm. Published data for potential standards for a ferri-heteropolytungstate could not be located for the visible spectral region

Neither of these standards has bands in the 490 nm region that

are as intense as those of the ophirite spectrum. Thus, it is likely that, if tetrahedral ferric iron were present in ophirite, its presence could not be confirmed by optical spectroscopic methods. The optical spectrum suggests four observations on Fe and Mn valence state: (1)  $Fe^{2+}$  is not present in ophirite, (2) Mn as  $Mn^{3+}$ is plausible in ophirite, (3) absorption caused by  $Mn^{2+}$  would be too weak to observe in the optical spectrum, and (4) absorption caused by tetrahedral  $Fe^{3+}$  would be difficult or impossible to observe in the optical spectrum. These results are consistent with the results of the structural optimization, which indicates that all species are in their fully oxidized states.

#### Raman spectroscopy

The Raman spectrum of ophirite was collected with a Renishaw M-1000 microRaman system with a 514.5 nm argon ion laser and a 100× objective that produced a spot of about 1.2  $\mu$ m diameter with a depolarizer in the beam directly above the sample. Power at the sample was raised from 0.5 to 5 mW with no visible sample damage.

The ophirite Raman spectrum in Figure 4 bears close resemblance to the spectra of the other heteropolytungstates, as described by Detusheva et al. (2003). The spectra are dominated by the W = O stretching in the 900–960 cm<sup>-1</sup> region. The W–O–W bridge vibrations that occur in the 800–500 cm<sup>-1</sup> region and the W–O vibrations in the 250–200 cm<sup>-1</sup> region are relatively weak.

## **CHEMICAL ANALYSIS**

Analyses of ophirite (14 on two crystals) were performed at the University of Utah on a Cameca SX-50 electron microprobe with four wavelength-dispersive spectrometers. Analytical conditions were 15 keV accelerating voltage, 10 nA beam current, and a beam diameter of 10  $\mu$ m. Counting times were 20 s for each element. Raw X-ray intensities were corrected for matrix effects with a  $\phi\rho(z)$  algorithm (Pouchou and Pichoir 1991).

Because insufficient material was available for a direct determination of  $H_2O$ , the amount of water in ophirite was calculated on the basis of 30 total cations (Ca+Mg+Zn+Mn+Fe+Sb+W), charge balance, and 116 O atoms pfu, as determined by the crystal-structure analysis (see below). The results are presented in Table 1. The empirical formula of ophirite on this basis is Ca<sub>1.73</sub>



FIGURE 3. Optical absorption spectrum of an  $\sim$ 14.2 µm thick crystal of ophirite taken in two extinction directions on a crystal face that is close to the direction of an optic axis.



**FIGURE 4.** Baseline-corrected Raman spectrum of a crystal of ophirite compared to spectra of heteropolytungstate chemicals from Barats et al. (2008) = top and Detusheva et al. (2003) = center.

 $Mg_{3.99}[Zn_{2.02}(Mn_{1.82}^{3+}Sb_{0.22}^{5+})(H_2O)_2(Fe_{2.34}^{3+})(W_{17.99})O_{68}] \cdot 45.95H_2O.$ Such a casting of the formula ignores the extensive substitution in the ophirite structure. There is complex substitution among the cation sites in ophirite, which was quantified using optimization methods (Wright et al. 2000); that substitution is discussed subsequently. The ideal formula of ophirite is  $Ca_2Mg_4[Zn_2Mn_2^{3+}]$  $(H_2O)_2(Fe^{3+}W_9O_{34})_2] \cdot 46H_2O.$ 

## X-RAY CRYSTALLOGRAPHY AND STRUCTURE DETERMINATION

Powder and single-crystal X-ray diffraction data for ophirite were obtained on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer using monochromatized MoKa radiation. The powder data presented in Table 2 for ophirite are in good agreement with those calculated from the structure data. Observed d

TABLE 1. Analytical results for ophirite

Const.	wt%	St.dev. (metal)	Ideal wt% <sup>a</sup>	Standard		
CaO	1.68	0.61	1.94	diopside		
MgO	2.79	0.09	2.78	diopside		
ZnO	2.86	0.36	2.81	Zn Metal		
Mn₂O₃	2.50	0.22	2.73	rhodonite		
$Fe_2O_3$	3.25	0.20	2.76	hematite		
Sb <sub>2</sub> O <sub>5</sub>	0.61	0.13	-	GaSb (syn)		
WO₃	71.94	1.01	72.06	W metal		
H₂O	15.24 <sup>b</sup>		14.92			
Total	100.87		100.00			
<sup>a</sup> Calculated using Ca-Mg/[Zn-Mn <sup>3+</sup> (H <sub>2</sub> O) <sub>2</sub> (Fe <sup>3+</sup> W <sub>2</sub> O <sub>22</sub> ) <sub>2</sub> ]-46H <sub>2</sub> O						

 $1_2^{-1}(\Pi_2 U)_2(I$ <sup>b</sup> Based on structure.

TABLE Z. FUWLELATAV UIITALIUTUALATUTUDI	וסח טמנמ וסר סנ	unifaction data	POwder A-ra	ABLE Z.
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values and intensities were derived by profile fitting using JADE 2010 software.

The Rigaku CrystalClear software package was used for reducing X-ray intensity data to structure factors, including corrections for Lorentz and polarization effects and the application of empirical absorption corrections; the structure was solved by direct methods using SIR2004 (Burla et al. 2005). The SHELXL-97 software (Sheldrick 2008) was used for the structure refinement, utilizing neutral-atom scattering factors. Hydrogen atoms were located using difference Fourier maps. O-H distances were restrained to be 0.90(2) Å, and H-H distances for each H<sub>2</sub>O were restrained to be 1.45(3) Å. The  $U_{eq}$  for each H was set to 1.2× that of O to which it is bonded. The occupancies of all non-H cations except Mg were released to determine the total electron counts at those sites, values used subsequently in the optimization of cation occupancies. Details of the data collection and structure refinement are provided in Table 3, and the atom coordinates and equivalent displacement parameters are in Table 4. Table 5 lists selected interatomic distances. A copy of anisotropic displacement parameters, a table of observed and calculated structure factors, and the CIF file for ophirite are on deposit and available as listed below.<sup>1</sup>

<sup>&</sup>lt;sup>1</sup> Deposit item AM-14-502, CIF. Deposit items are stored on the MSA web site and available via the American Mineralogist Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam. org), and then click on the deposit link

obs	$d_{\rm obs}$	$d_{calc}$	$I_{calc}$	hkl	$I_{obs}$	$d_{\rm obs}$	$d_{\rm calc}$	I <sub>calc</sub>	hkl	$I_{obs}$	$d_{\rm obs}$	$d_{\rm calc}$	I <sub>calc</sub>	hkl
38	16.72	16.5383	45	001			2.6365	5	401		(	1.7298	1	145
01	11 33 ∫	11.2739	100	011	33	2 504	2.5916	3	413		]	1.7283	1	<u>2</u> ·3·10
51	11.55 L	11.2164	19	010	55	2.394	2.5822	6	345	14	1.722	1.7241	4	1.2.10
100	10.69 \$	10.8185	52	100			2.5690	3	141			1.7208	1	468
100	10.09 1	10.2594	51	110	7	2.506	2.5087	6	144			1.7140	2	407
		9.8552	8	111	17	2 202	<b>\$</b> 2.3829	6	414	4	1 685	1.6842	2	418
		9.3972	15	101	17	2.382	<b>l</b> 2.3562	5	403	-	1.005	. 1.6811	2	271
55	8.27	8.2692	56	002	r	2 2 2 0	<b>\$</b> 2.2340	2	146		1	1.6580	1	751
		8.0735	15	011	5	2.239	<b>1</b> 2.2302	3	207			1.6561	1	263
12	601 5	5.9994	4	122	10	2 176	<b>\$</b> 2.1824	3	142	11	1.651	1.6545	1	3.3.10
12	0.04 l	5.9786	5	021	12	2.176	<b>l</b> 2.1655	6	017		)	1.6501	1	2.2.10
33	5.44	5.4408	10	$\overline{2} \overline{1} 1$	6	2 1 1 7	<b>\$</b> 2.1247	2	128			1.6487	3	753
7	5 20 <b>S</b>	5.2750	9	221	0	2.117	<b>l</b> 2.1108	2	420		1	1.6446	2	653
/	<sup>3.30</sup> l	5.2646	9	201			2.0797	2	463		1	1.6186	2	285
7	4.825	4.8267	6	0 2 1	6	2.067	2.0692	1	335			1.6147	2	055
16	4.519	4.4889	6	121	0	2.007	2.0673	1	008			1.6115	1	577
10	1 22E S	4.3412	7	132			2.0635	1	161	20	1.612	1.6105	1	347
10	4.555 <b>l</b>	4.2964	6	122			2.0012	1	416			1.6023	1	070
	(	4.1359	9	124	6	1.992	1.9967	1	338			1.6008	2	146
77	4 1 1 0	4.1133	2	130			1.9892	1	136			1.5998	3	318
27	4.119	4.1007	3	232			1.9230	1	036	10	1.588	1.5837	5	356
	L L	4.0909	3	212			1.9217	1	643		(	1.5608	3	1.3.11
	(	3.6208	7	312			1.9133	2	345	20	1 554	1.5589	2	527
15	3.588	3.6066	4	231	33	1,916	1.9119	1	610	20	1.554	1.5472	3	713
	(	3.5484	6	124	55		1.9089	3	307		(	1.5368	3	648
13	3.464	3.4673	12	301			1.9058	1	129		(	1.5021	3	753
3	3.319	3.3077	7	005			1.9047	1	316	11	1.498	1.5000	2	429
30	3.190	3.1993	15	133			1.8989	4	432		(	1.4952	2	2.7.10
75	2.992	3.0196	6	334			<b>(</b> 1.8596	3	653	10	1 100 \$	1.4680	2	443
		2.9947	16	341	18	1.856	1.8530	2	612	10	1.400	. 1.4673	3	686
		2.9462	9	115			1.8513	3	434		(	1.4483	1	2.3.12
10	2012	2.9150	7	303			1.8071	4	522	2	1 4 4 2	1.4429	1	272
16	2.913 <b>(</b>	2.9107	17	015			1.8047	1	229	3	1.443	1.4423	2	680
	(	2.7645	8	412			1.8039	1	515		(	1.4418	1	715
55	2.760	2.7564	21	006	15	1.799	1.8009	1	067					
	l	2.7522	11	135			1.7943	1	137					
		2.7102	9	341			1.7933	1	276					
							1.7916	1	165					

Notes: Only calculated lines with intensities greater than 7 are listed unless they correspond to observed lines. Mismatches in intensities between observed and calculated lines are due to the large number of lines of relatively low intensity that are not listed.

Sample and crystal data for ophirite TARLE 3

TABLE J. Sample and cry	star data for opfinite				
Formula weight	5726.57				
Temperature	293(2) K				
Wavelength	0.71075 Å				
Crystal size	$0.040 \times 0.090 \times 0.100 \text{ mm}$				
Crystal system	Triclinic				
Space group	PĪ				
Unit-cell dimensions	$a = 11.9860(2)$ Å $\alpha = 69.690(5)^{\circ}$				
	$b = 13.2073(2)$ Å $\beta = 85.364(6)^{\circ}$				
	$c = 17.6891(12) \text{ Å} \qquad \gamma = 64.875(5)^{\circ}$				
Volume	2370.35(18) Å <sup>3</sup>				
Absorption coefficient	22.543 mm <sup>-1</sup>				
F <sub>000</sub>	2579				
Theta range	3.0 to 27.46°				
Index ranges	–15 ≤ <i>h</i> ≤ 15, –17 ≤ <i>k</i> ≤ 17, –22 ≤ <i>l</i> ≤ 22				
Reflections collected	76304				
Independent reflections	$10834 [R_{int} = 0.0578]$				
Completeness	99.8%				
Max. and min. transmission	0.4658 and 0.2114				
Structure solution	direct methods				
Structure solution program	SHELXS-97 (Sheldrick 2008)				
Refinement method	Full-matrix least-squares on F <sup>2</sup>				
Refinement program	SHELXL-97 (Sheldrick 2008)				
Function minimized	$\Sigma w (F_0^2 - F_c^2)^2$				
Data/restraints/parameters	10834/72/802				
Goodness-of-fit on F <sup>2</sup>	1.034				
$\Delta / \sigma_{max}$	0.002				
Final R indices	9230 data; $l > 2\sigma(l)$ $R_1 = 0.0298$ , $wR_2 = 0.0671$				
	all data $R_1 = 0.0386, wR_2 = 0.0704$				
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0338P)^2 + 11.0210P]$				
5 5	where $P = (F_0^2 + 2F_c^2)/3$				
Largest diff. peak and hole	2.059 and −1.388 e×Å- <sup>3</sup>				

**TABLE 4.** Atomic coordinates and equivalent isotropic displacement

	naramotor fo	ar atoms in onbi	rito		H42A	0.525(10)	0.465(9)	0.140(4)	
	parameterit		nie		H42B	0.494(11)	0.425(10)	0.223(3)	
	x/a	y/b	z/c	$U_{eq}^{a}$	043	0.5905(7)	0.3576(6)	0.0292(4)	0
M1	0.89860(8)	0.63418(7)	0.32977(5)	0.01612(17)	H43A	0.534(6)	0.372(9)	-0.010(4)	
M2	0.97962(8)	0.61798(7)	0.51246(5)	0.02115(18)	H43B	0.665(4)	0.318(9)	0.012(5)	
M3	0.74884(9)	0.56532(8)	0.49729(6)	0.0269(2)	044	0.5380(8)	0.1689(6)	0.2588(4)	
M4	0.2029(2)	0.0955(2)	0.15709(14)	0.0242(5)	H44A	0.489(8)	0.187(8)	0.298(4)	
M5	0.5557(3)	0.2693(2)	0.14317(18)	0.0368(6)	H44B	0.595(7)	0.093(4)	0.280(5)	
M6	0.72573(18)	0.12204(16)	0.47144(11)	0.0345(4)	O45	0.3699(8)	0.3200(8)	0.1117(6)	
W1	0.62958(3)	0.59597(3)	0.305958(18)	0.02324(7)	H45A	0.345(11)	0.261(8)	0.139(6)	
W2	0.68205(3)	0.79959(3)	0.153583(17)	0.02192(7)	H45B	0.402(11)	0.299(10)	0.067(5)	
W3	0.59807(3)	0.84097(3)	0.329077(18)	0.02213(7)	O46	0.7354(6)	0.2284(6)	0.1832(4)	0
W4	0.14645(3)	0.70577(3)	0.33653(17)	0.02102(7)	H46A	0.771(7)	0.279(6)	0.158(6)	
W5	0.95150(3)	0.86633(3)	0.173366(17)	0.02129(7)	H46B	0.800(6)	0.155(4)	0.197(6)	
W6	0.87027(3)	0.89918(2)	0.350128(17)	0.02192(7)	O47	0.8161(9)	0.0425(8)	0.6050(5)	
W7	0.00624(3)	0.58314(3)	0.144552(17)	0.02216(7)	H47A	0.861(8)	0.076(10)	0.616(8)	
W8	0.94939(3)	0.37895(3)	0.294331(17)	0.02156(7)	H47B	0.736(4)	0.088(10)	0.608(9)	
W9	0.19665(3)	0.42058(3)	0.309721(17)	0.02161(7)	O48	0.5116(8)	0.1655(8)	0.4577(5)	
01	0.7321(4)	0.7060(4)	0.2866(3)	0.0210(10)	H48A	0.501(11)	0.102(7)	0.455(6)	
02	0.9553(4)	0.7555(4)	0.3003(3)	0.0209(10)	H48B	0.495(11)	0.167(9)	0.508(3)	
03	0.9977(4)	0.5250(4)	0.2781(3)	0.0197(10)	O49	0.6677(7)	0.2764(6)	0.3417(4)	0
04	0.9122(4)	0.5581(4)	0.4444(3)	0.0218(10)	H49A	0.703(8)	0.251(7)	0.301(4)	
05	0.8794(5)	0.7852(4)	0.4474(3)	0.0246(11)	H49B	0.614(8)	0.353(4)	0.320(5)	
06	0.0426(5)	0.6511(4)	0.5971(3)	0.0250(11)	O50	0.0769(7)	0.8691(7)	0.5375(5)	0
07	0.1226(5)	0.6184(4)	0.4410(3)	0.0247(11)	H50A	0.082(9)	0.809(7)	0.523(7)	
D8	0.1641(5)	0.3971(4)	0.4185(3)	0.0253(11)	H50B	0.002(5)	0.900(8)	0.555(7)	
09	0.6865(5)	0.5239(5)	0.4098(3)	0.0289(12)	O51	0.6507(7)	0.3100(6)	0.4984(4)	0
D10	0.6509(5)	0.7451(5)	0.4316(3)	0.0286(12)	H51A	0.591(7)	0.384(4)	0.479(5)	
D11	0.5286(5)	0.5364(5)	0.2978(3)	0.0303(12)	H51B	0.634(9)	0.272(7)	0.548(3)	
012	0.5141(5)	0.7428(5)	0.3179(3)	0.0291(12)	052	0.7192(8)	0.9252(6)	0.5346(5)	
D13	0.7827(5)	0.4838(5)	0.2756(3)	0.0275(11)	H52A	0.658(7)	0.997(4)	0.514(7)	
014	0.6050(5)	0.6960(4)	0.1843(3)	0.0266(11)	H52B	0.702(10)	0.872(6)	0.524(7)	
015	0.6168(6)	0.8799(5)	0.0549(3)	0.0340(13)	O53	0.4133(7)	0.4275(7)	0.9084(5)	0
D16	0.5731(5)	0.9049(4)	0.2047(3)	0.0247(11)	H53A	0.448(8)	0.358(6)	0.953(4)	
017	0.8326(5)	0.6755(4)	0.1391(3)	0.0252(11)	H53B	0.330(4)	0.457(8)	0.920(6)	
D18	0.7967(5)	0.8715(4)	0.1578(3)	0.0270(11)	054	0.1818(7)	0.5998(8)	0.9065(5)	
019	0.4642(5)	0.9581(5)	0.3392(4)	0.0382(14)	H54A	0.144(9)	0.602(10)	0.953(4)	
020	0.7123(5)	0.9098(5)	0.3169(3)	0.0284(12)	H54B	0.148(9)	0.567(10)	0.882(5)	
D21	0.2886(5)	0.7037(5)	0.3521(3)	0.0315(12)	055	0.6599(8)	0.3241(9)	0.8424(6)	
022	0.1959(5)	0.5725(4)	0.3038(3)	0.0250(11)	H55A	0.672(10)	0.371(10)	0.866(8)	
023	0.1154(5)	0.8141(5)	0.2224(3)	0.0272(11)	H55B	0.738(5)	0.285(10)	0.828(8)	
024	0.0454(5)	0.8539(4)	0.3621(3)	0.0240(11)	056	0.8373(9)	0.2245(8)	0.0022(6)	
025	0.9623(6)	0.9683(5)	0.0834(3)	0.0348(13)	H56A	0.867(12)	0.226(9)	-0.046(4)	
026	0.0207(5)	0.7209(4)	0.1488(3)	0.0244(11)	H56B	0.864(12)	0.148(4)	0.035(5)	
027	0.8823(5)	0.9761(4)	0.2318(3)	0.0254(11)	057	0.6333(8)	0.1289(7)	0.9588(5)	
D28	0.8154(5)	0.0273(5)	0.3747(3)	0.0314(12)	H57A	0.646(11)	0.115(9)	1.011(2)	
029	0.0296(6)	0.5985(5)	0.0440(3)	0.0348(13)	H57B	0.658(10)	0.184(8)	0.928(5)	
030	0.1752(5)	0.4874(4)	0.1891(3)	0.0253(11)	058	0.5965(6)	0.5614(6)	0.5611(4)	0
031	0.9749(5)	0.4413(4)	0.1759(3)	0.0273(12)	H58A	0.518(4)	0.616(6)	0.548(5)	
032	0.9489(5)	0.2500(5)	0.2893(3)	0.0304(12)	H58B	0.601(7)	0.515(6)	0.612(3)	
233	0.1392(5)	0.3097(4)	0.3052(3)	0.0255(11)	$U_{eq}$ is defi	ined as one third of t	he trace of the orthog	jonalized U <sub>ij</sub> tensor.	
					<u> </u>				

## **DESCRIPTION OF THE STRUCTURE**

Ophirite is a bipartite structure that consists of a structural unit and an interstitial unit, as elucidated by Schindler and Hawthorne (2001). The  $\{ {}^{[6]}Zn_2{}^{[6]}Mn_2^{3+}(H_2O)_2({}^{[4]}Fe^{3+[6]}W_9^{6+}O_{34})_2 \} ^{12-}$  heteropolyanion defines the structural unit, the anionic portion of the structure. The more rigid structural units are linked by the interstitial unit, the cationic portion of the structure, with bonds of lower

y/b

z/c

TABLE	4.—	CONTINUED

x/a

	70 G	), 0	2/0	C Ed
034	0.3551(5)	0.3334(5)	0.3164(3)	0.0335(13)
025	0.2672(5)	0.0020(5)	0.1090(2)	0.0244(12)
035	0.3072(3)	0.0920(5)	0.1000(3)	0.03++(13)
H35A	0.429(6)	0.027(5)	0.139(4)	0.041
H35B	0.367(8)	0.095(7)	0.058(2)	0.041
036	0.2537(5)	0 1214(5)	0.2560(4)	0.0366(14)
030	0.2337(3)	0.1214(5)	0.2300(4)	0.0500(14)
H36A	0.332(4)	0.080(6)	0.277(5)	0.044
H36B	0.219(6)	0.188(5)	0.269(5)	0.044
037	0.2893(6)	0.9127(5)	0 2153(4)	0.0422(15)
11274	0.2000(0)	0.9127(3)	0.2133(4)	0.0422(15)
H3/A	0.220(4)	-0.081(9)	0.238(5)	0.051
H37B	0.351(5)	-0.116(8)	0.253(4)	0.051
038	0.0402(6)	0.0990(6)	0.2066(4)	0.0404(15)
0.50	0.0402(0)	0.0550(0)	0.2000(4)	0.0404(13)
H38A	0.002(7)	0.055(7)	0.203(5)	0.048
H38B	0.091(7)	0.054(7)	0.252(4)	0.048
039	0 1247(6)	0.2796(5)	0 1008(4)	0.0387(14)
11204	0.1247(0)	0.27 50(5)	0.1000(4)	0.0507(14)
H39A	0.076(7)	0.301(7)	0.060(4)	0.046
H39B	0.101(8)	0.323(7)	0.132(4)	0.046
040	0 1533(6)	0.0698(7)	0.0582(4)	0.0485(17)
1140.4	0.212(5)	0.014(7)	0.042(6)	0.050
H4UA	0.213(5)	0.014(7)	0.043(6)	0.058
H40B	0.079(4)	0.088(8)	0.040(6)	0.058
041	0.6199(7)	0 1202(6)	0 1149(4)	0.0518(18)
	0.635(0)	0.046(4)	0.146(E)	0.062
H41A	0.055(9)	0.040(4)	0.146(5)	0.062
H41B	0.551(6)	0.148(7)	0.080(5)	0.062
042	0.4899(8)	0.4193(6)	0.1739(5)	0.060(2)
4124	0.525(10)	0.465(0)	0.140(4)	0.072
H4ZA	0.525(10)	0.405(9)	0.140(4)	0.072
H42B	0.494(11)	0.425(10)	0.223(3)	0.072
043	0.5905(7)	0.3576(6)	0.0292(4)	0.0503(17)
L 42 A	0 E34(6)	0.372(0)	0.010(4)	0.06
TH3A	0.554(6)	0.372(9)	-0.010(4)	0.00
H43B	0.665(4)	0.318(9)	0.012(5)	0.06
044	0.5380(8)	0.1689(6)	0.2588(4)	0.059(2)
	0.490(9)	0 107(0)	0.208(4)	0.07
П44А	0.469(6)	0.167(6)	0.296(4)	0.07
H44B	0.595(7)	0.093(4)	0.280(5)	0.07
045	0.3699(8)	0.3200(8)	0.1117(6)	0.070(2)
	0 245(11)	0.261(9)	0.120(6)	0.094
H45A	0.545(11)	0.201(8)	0.139(6)	0.064
H45B	0.402(11)	0.299(10)	0.067(5)	0.084
046	0.7354(6)	0.2284(6)	0.1832(4)	0.0468(16)
L16A	0 771(7)	0.270(6)	0 159(6)	0.056
1140A	0.771(7)	0.279(0)	0.138(0)	0.050
H46B	0.800(6)	0.155(4)	0.197(6)	0.056
047	0.8161(9)	0.0425(8)	0.6050(5)	0.078(3)
H47A	0.861(8)	0.076(10)	0.616(8)	0.003
1147.4	0.001(0)	0.070(10)	0.010(0)	0.095
H4/B	0.736(4)	0.088(10)	0.608(9)	0.093
O48	0.5116(8)	0.1655(8)	0.4577(5)	0.064(2)
H18A	0 501(11)	0 102(7)	0.455(6)	0.077
11407	0.501(11)	0.102(7)	0.433(0)	0.077
H48B	0.495(11)	0.167(9)	0.508(3)	0.077
049	0.6677(7)	0.2764(6)	0.3417(4)	0.0520(18)
H49A	0 703(8)	0.251(7)	0 301(4)	0.062
11400	0.705(0)	0.257(7)	0.301(4)	0.002
H49B	0.614(8)	0.353(4)	0.320(5)	0.062
O50	0.0769(7)	0.8691(7)	0.5375(5)	0.0561(18)
H50A	0.082(9)	0.809(7)	0 523(7)	0.067
LICOD	0.002(5)	0.000(0)	0.525(7)	0.007
HOUR	0.002(5)	0.900(8)	0.555(7)	0.067
051	0.6507(7)	0.3100(6)	0.4984(4)	0.0539(18)
H51A	0 591(7)	0 384(4)	0.479(5)	0.065
	0.634(0)	0.272(7)	0 549(2)	0.065
11515	0.034(9)	0.272(7)	0.348(3)	0.005
052	0./192(8)	0.9252(6)	0.5346(5)	0.066(2)
H52A	0.658(7)	0.997(4)	0.514(7)	0.079
157P	0.702(10)	0.972(6)	0.524(7)	0.070
052	0.702(10)	0.072(0)	0.524(7)	0.079
053	0.4133(7)	0.4275(7)	0.9084(5)	0.0589(19)
H53A	0.448(8)	0.358(6)	0.953(4)	0.071
H53B	0.330(4)	0.457(8)	0.920(6)	0.071
054	0.1010(7)	0.457(0)	0.020(0)	0.071
054	0.1818(7)	0.5998(8)	0.9065(5)	0.062(2)
H54A	0.144(9)	0.602(10)	0.953(4)	0.074
H54B	0.148(9)	0.567(10)	0.882(5)	0.074
055	0.6500(9)	0.2241(0)	0.9424(6)	0.070(2)
000	0.0399(0)	0.3241(9)	0.0424(0)	0.079(5)
H55A	0.672(10)	0.371(10)	0.866(8)	0.095
H55B	0,738(5)	0,285(10)	0.828(8)	0.095
056	0 8372/0)	0.22/5/0)	0.0022(6)	0.070/2)
030	0.0373(9)	0.2243(0)	0.0022(0)	0.076(3)
H56A	0.867(12)	0.226(9)	-0.046(4)	0.094
H56B	0.864(12)	0.148(4)	0.035(5)	0 094
057	0.6222(9)	0 1280(7)	0.0599(5)	0.060(2)
0.57	0.0333(0)	0.1209(/)	(2)00(2)	0.000(2)
H57A	0.646(11)	0.115(9)	1.011(2)	0.072
H57B	0.658(10)	0.184(8)	0.928(5)	0.072
058	0 5965(6)	0.5614(6)	0.5611(4)	0.0407(15)
0.00	(0) 202020	0.3014(0)	0.3011(4)	0.0407(15)
H58A	0.518(4)	0.616(6)	0.548(5)	0.049
H58B	0.601(7)	0.515(6)	0.612(3)	0.049

 $U_{eq}^{a}$ 

bond-valence linking Mg and Ca to an O atom of the structural unit and/or interstitial H<sub>2</sub>O groups. The interstitial unit in ophirite,  $\{[Mg(H_2O)_6]_4[Ca(H_2O)_6]_2 \cdot 10H_2O\}^{12+}$ , balances the charge of the structural unit and links the structural units together. The atomic arrangement of ophirite is depicted in Figure 5.

## The ${[6]Zn_2[6]Mn_2^{3+}(H_2O)_2([4]Fe^{3+[6]}W_9^{6+}O_{34})_2}^{12-}$ structural unit

The structural unit in ophirite consists of the  $\{{}^{6|}Zn_2$  ${}^{[6]}Mn_2^{3+}(H_2O)_2({}^{[4]}Fe^{3+[6]}W_9^{6+}O_{34})_2\}^{12-}$  polyanion (Fig. 6). That polyanion is formed of two ( ${}^{[4]}Fe^{3+[6]}W_9^{6+}O_{34}$ ) groups (Fig. 7), with an intervening  $Zn_2Mn_2^{3+}(H_2O)_2$  edge-sharing octahedral layer formed of two  $Mn^{3+}O_6$  and two  $ZnO_5(H_2O)_1$  octahedra that share oxygen atoms with the ( ${}^{[4]}Fe^{3+[6]}W_9^{6+}O_{34}$ ) groups. Although ophirite is the first known mineral to contain the ( ${}^{[4]}Fe^{3+[6]}W_9^{6+}O_{34}$ ) group, the { $XM_9O_{34}$ } heteropolyanion is well known in synthetic compounds.

Keggin (1934) was the first to solve the atomic arrangement of the heteropolyanionic  $(XM_{12}O_{40})$  group, using X-ray diffraction methods. Now known as the Keggin heteropolyanion, the heteropoly acid is formed of 12 M-O octahedra surrounding a central tetrahedral cation, X; the most common M cations are Mo and W. The Keggin heteropolyanion is also known to spawn defect structures in which one or more of the octahedra are removed from the (XM<sub>12</sub>O<sub>40</sub>) Keggin anion, such as (XM<sub>11</sub>O<sub>39</sub>), a defect structure in which one octahedron is absent from the Keggin anion, and the  $(XM_9O_{34})$  group, a defect structure in which three octahedra are absent from the Keggin anion. Such heteropolyanions are known as "lacunary Keggin structures" to note the defect structures caused by the missing octahedra; the  $(XM_9O_{34})$  group is also known as a "tri-lacunary" because of the deficiency of three octahedra. A rich literature exists on the chemistry and structure of lacunary Keggin anions.

The heteropolytungstate (<sup>[4]</sup>Fe<sup>3+[6]</sup>W<sub>9</sub><sup>6+</sup>O<sub>34</sub>) in ophirite is a trilacunary Keggin anion of the  $\alpha$ -B-(XM<sub>9</sub>O<sub>34</sub>) type, and it forms the foundation of the structural unit in ophirite. In ophirite, two of the {XM<sub>9</sub>O<sub>34</sub>} tri-lacunary Keggin anions (X = Fe<sup>3+</sup>, M = W<sup>6+</sup>; Fig. 7) create a "sandwich" structure with four intervening coplanar edge-sharing octahedra (2 × {(Mn<sup>3+</sup>O<sub>6</sub>)+[ZnO<sub>5</sub>(H<sub>2</sub>O)<sub>1</sub>]}) between opposing {Fe<sup>3+</sup>W<sub>9</sub>O<sub>34</sub>} groups, yielding the structural unit of {<sup>[6]</sup>Zn<sub>2</sub><sup>[6]</sup>Mn<sub>3</sub><sup>3+</sup>(H<sub>2</sub>O)<sub>2</sub>(<sup>[4]</sup>Fe<sup>3+[6]</sup>W<sub>9</sub><sup>6+</sup>O<sub>34</sub>)<sub>2</sub>}<sup>12-</sup> depicted in Figure 6. Although ophirite is the first example of the tri-lacunary polyanion in minerals, the sandwich structure with four intervening octahedra between two tri-lacunary Keggin anions is well known in synthetic compounds (e.g., Li et al. 2009; Limanski et al. 2002; Bösing et al. 1997 and references therein).

## The $\{[Mg(H_2O)_6]_4[Ca(H_2O)_6]_2 \cdot 10H_2O\}^{12+}$ interstitial unit

As noted by Schindler and Hawthorne (2001), the charge of the anionic structural units is balanced by the cationic interstitial unit. The interstitial unit in the structure of ophirite is formed of two distinct Mg(H<sub>2</sub>O)<sub>6</sub> octahedra and a Ca(H<sub>2</sub>O)<sub>6</sub>O<sub>1</sub> polyhedron, as well as five isolated water molecules. Note that the oxygen atom of the Ca(H<sub>2</sub>O)<sub>6</sub>O<sub>1</sub> polyhedron is shared with one of the W octahedra of the structural unit, whereas the remainder of the linkage between the structural unit and the interstitial unit is attained through hydrogen bonding. The complete interstitial unit (not including the oxygen atom shared with the structural unit) has a composition of {[Mg(H<sub>2</sub>O)<sub>6</sub>]<sub>4</sub>[Ca(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>·10H<sub>2</sub>O}<sup>12+</sup>,

**TABLE 5.** Selected bond distances for atoms in ophirite

M1-02	1.894(5)	M2-05	1.963(5)	M3-010	2.074(5)
01	1.898(5)	06	1.979(5)	O58	2.079(6)
03	1.900(5)	04	2.010(5)	O4	2.079(5)
04	1.911(5)	O4'	2.022(5)	09	2.091(5)
Mean	1.901	07	2.047(5)	07	2.171(5)
		08	2.069(5)	08	2.181(5)
		Mean	2.015	Mean	2.113
M4-038	2.061(6)	M5-041	2.014(7)	M6-047	2.363(8)
O40	2.069(6)	042	2.047(7)	O28	2.386(6)
037	2.069(6)	O43	2.059(7)	O49	2.390(7)
O35	2.076(6)	O44	2.067(7)	O48	2.393(9)
O36	2.076(6)	045	2.095(9)	O50	2.407(8)
O39	2.079(6)	O46	2.104(7)	O51	2.461(7)
Mean	2.072	Mean	2.064	O52	2.480(8)
				Mean	2.411
W1-011	1.739(5)	W2-015	1.736(5)	W3-019	1.743(5)
09	1.785(5)	014	1.870(5)	O10	1.790(5)
012	1.918(5)	016	1.897(5)	O20	1.903(5)
013	1.983(5)	O17	1.927(5)	O12	2.013(5)
014	2.064(5)	O18	1.992(5)	O16	2.061(5)
O1	2.200(5)	01	2.236(5)	O1	2.151(5)
Mean	1.948	Mean	1.943	Mean	1.944
W4-021	1.735(6)	W5-025	1.729(5)	W6-028	1.734(5)
07	1.882(5)	O18	1.867(5)	O5	1.825(5)
O22	1.884(5)	O27	1.933(5)	O24	1.930(5)
023	1.982(5)	O26	1.933(5)	O20	1.961(5)
024	2.001(5)	O23	1.949(5)	O27	2.008(5)
02	2.182(5)	02	2.206(5)	O2	2.188(5)
Mean	1.944	Mean	1.936	Mean	1.941
W7-029	1.732(5)	W8-032	1.739(5)	W9-034	1.741(5)
017	1.903(5)	O6	1.824(5)	O8	1.876(5)
026	1.926(5)	O13	1.860(5)	O33	1.890(5)
O30	1.927(5)	O31	2.018(5)	O22	1.968(5)
031	1.950(5)	O33	2.057(5)	O30	1.997(5)
O3	2.225(4)	O3	2.162(5)	O3	2.188(5)
Mean	1.944	Mean	1.943	Mean	1.943



FIGURE 5. Atomic arrangement of ophirite down [100]. Red polyhedra are WO<sub>6</sub> octahedra, orange are  $Mn^{3+}O_6$  octahedra, green are  $ZnO_5(H_2O)^1$  octahedra, and yellow is the  $Fe^{3+}O_4$  tetrahedron of the structural unit. For the interstitial unit, Mg(H<sub>2</sub>O)<sub>6</sub> octahedra are shown in blue, and the [Ca(H<sub>2</sub>O)<sub>6</sub>O] polyhedra are shown as ball and stick. Isolated water molecules of the interstitial unit are also shown.

balancing the charge of the structural unit with its extensive cation substitutions, and yielding the simplified structural formula  $\{[Mg(H_2O)_6]_4[Ca(H_2O)_6]_2 \cdot 10H_2O\}^{12+} \{Zn_2Mn_2^{3+}(H_2O)_2(Fe_2^{3+}W_{18}O_{68})\}^{12-}$  for ophirite.

## **Cation substitution**

The extensive substitution among the cations and cation sites in ophirite was elucidated using the program OccQP (Wright



FIGURE 6.  ${Zn_2Mn_2^{2+}(H_2O)_2}$ (<sup>[4]</sup>Fe<sup>3+[6]</sup>W<sub>9</sub><sup>6+</sup>O<sub>34</sub>)<sub>2</sub>)<sup>12–</sup> structural unit in ophirite. Colors as in Figure 5. The structural unit is formed of two tri-lacunary Keggin structures sandwiching the octahedral layer of four octahedra.



FIGURE 7. [<sup>[4]</sup>F $e^{3+}$ <sup>[6]</sup>W $_9^{6+}O_{34}$ ]<sup>11-</sup> portion of the { $Zn_2Mn_2^{3+}(H_2O)_2(^{[4]}Fe^{3+}$ <sup>[6]</sup>W $_9^{6+}O_{34})_2$ }<sup>12-</sup> structural group in ophirite, a tri-lacunary Keggin structure. The polyanion is formed of nine WO<sub>6</sub> octahedra with a central Fe<sup>3+</sup>O<sub>4</sub> tetrahedron; colors as in previous figures.

et al. 2000), which uses a constrained leastsquares formulation to optimize occupancy assignments based upon site scattering, chemical composition, charge balance, bond valence and cation-anion bond lengths. The results of the optimization are provided in Table 6. Those results demonstrate the extensive cation solution in both the structural

б.	Site occupants for cation sites
	in onhirite

	opinite
ation site	Site occupants
<i>N</i> 1	Fe <sup>3+</sup> <sub>0.80</sub> Sb <sup>5+</sup> <sub>0.11</sub> Ca <sub>0.07</sub> Mg <sub>0.02</sub>
/12	Mn <sup>3+</sup> <sub>0.71</sub> Sb <sup>5+</sup> <sub>0.16</sub> Fe <sup>3+</sup> <sub>0.12</sub> W <sub>0.01</sub>
//3	Zn <sub>0.58</sub> Fe <sup>3+</sup> <sub>0.34</sub> Ca <sub>0.07</sub> Sb <sup>5+</sup> <sub>0.01</sub>
//4	Mg <sub>0.99</sub> Mn <sup>3+</sup>
15	Mg <sub>0.99</sub> Mn <sup>3+</sup> <sub>0.01</sub>
16	Ca <sub>0.73</sub> Mg <sub>0.25</sub> Zn <sub>0.02</sub>
V1	W <sub>0.96</sub> Mn <sup>3+</sup> <sub>0.04</sub>
V2	W <sub>0.96</sub> Mn <sup>3+</sup> <sub>0.04</sub>
V3	W <sub>0.96</sub> Mn <sup>3+</sup> <sub>0.04</sub>
V4	W <sub>0.96</sub> Mn <sup>3+</sup> <sub>0.04</sub>
V5	W <sub>0.98</sub> Mn <sup>3+</sup> <sub>0.02</sub>
V6	W <sub>0.97</sub> Mn <sup>3+</sup> <sub>0.03</sub>
V7	W <sub>0.98</sub> Mn <sup>3+</sup> <sub>0.02</sub>
V8	W <sub>0.98</sub> Mn <sup>3+</sup> <sub>0.02</sub>
V9	W <sub>0.97</sub> Mn <sup>3+</sup> <sub>0.03</sub>

unit and interstitial unit, which yields the charge balance in ophirite. The method was also used to determine the "best-fit" valence state for Fe and Mn, as the program was free to vary the valence state of these cations during the minimization process; as expected, all Fe was found to be  $Fe^{3+}$ , and the Mn results are in accord with the optical spectroscopic results that are consistent with all Mn as  $Mn^{3+}$ .

The simplified structural formula for ophirite can be written: {[Mg(H<sub>2</sub>O)<sub>6</sub>]<sub>4</sub>[Ca(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>·10H<sub>2</sub>O} {Zn<sub>2</sub>Mn<sub>2</sub><sup>3+</sup>(H<sub>2</sub>O)<sub>2</sub> (Fe<sub>2</sub><sup>3+</sup>W<sub>18</sub>O<sub>68</sub>)}. Given the results of the optimization, the parallel detailed structural formula for ophirite can be written as: {[(Mg,Mn)(H<sub>2</sub>O<sub>6</sub>)]<sub>4</sub>[(Ca,Mg,Zn)(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>·10H<sub>2</sub>O} {(Zn,Fe<sup>3+</sup>,Ca,Sb<sup>5+</sup>)<sub>22.00</sub> (Mn<sup>3+</sup>,Sb<sup>5+</sup>,Fe<sup>3+</sup>,W)<sub>22.00</sub> (H<sub>2</sub>O)<sub>2</sub> [(Fe<sup>3+</sup>,Sb<sup>5+</sup>,Ca,Mg)<sub>22.00</sub>(W<sup>6+</sup>,Mn<sup>3+</sup>)<sub>218.00</sub>O<sub>68</sub>]}. The quantification of the substitutions is given in Table 6.

## **IMPLICATIONS**

Many complex heteropolyanions have been synthesized, and they have long been used in industry and as catalysts in chemical processes. The most widely known heteropolyanion is the Keggin anion, for which a large body of literature exists. Until now, minerals containing the Keggin anion were not known to occur. Ophirite is the first known mineral to contain a lacunary defect derivative of the Keggin anion and its description introduces that polyanion and its associated structural groups to the mineralogical literature. The occurrence of ophirite demonstrates the natural conditions under which Keggin anions can form, and suggests that other members of this class of compounds occur naturally.

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