# Ferraioloite, MgMn<sup>2+</sup><sub>4</sub>(Fe<sup>2+</sup><sub>0.5</sub>Al<sup>3+</sup><sub>0.5</sub>)<sub>4</sub>Zn<sub>4</sub>(PO<sub>4</sub>)<sub>8</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>20</sub>, a new secondary phosphate mineral from the Foote mine, USA

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Abstract: Ferraioloite, MgMn<sup>2+</sup><sub>4</sub>(Fe<sup>2+</sup><sub>0.5</sub>Al<sup>3+</sup><sub>0.5</sub>)<sub>4</sub>Zn<sub>4</sub>(PO<sub>4</sub>)<sub>8</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>20</sub>, is a new secondary phosphate mineral from the Foote Lithium Company mine, Kings Mountain district, Cleveland County, North Carolina, USA. The mineral was found in tiny vughs within a thin seam of very fine-grained, sugary pegmatite with vivianite, fairfieldite/messelite, phosphophyllite, scholzite/ parascholzite, rittmannite, mangangordonite, kingsmountite, kastningite and metaswitzerite. Ferraioloite crystals occur as very thin greenish grey to lemon yellow plates or blades up to about 0.2 mm in length, but no more than a few µm thick. Crystals are biaxial (-), with indices of refraction  $\alpha = 1.575$ (calc),  $\beta = 1.5825(5)$ ,  $\gamma = 1.5835(5)$ , 2V(meas.) = 40(5)°. Dispersion is weak: r > v, the orientation is:  $X \approx \mathbf{a}$ ,  $Y = \mathbf{b}$ ,  $Z \approx \mathbf{c}$  and pleochroism: X, Z = colourless, Y = blue grey;  $Y >> X \approx Z$ . The empirical formula (based on 56 O atoms pfu) is Ca<sub>0.21</sub>Mg<sub>0.50</sub>Mn<sup>2+</sup><sub>4.16</sub>Fe<sup>2+</sup><sub>2.05</sub>Al<sup>3+</sup><sub>2.01</sub>Zn<sub>4.27</sub>P<sub>8.00</sub>H<sub>43.59</sub>O<sub>56</sub>. Ferraioloite is monoclinic, space group *I2/m*, with the unit-cell parameters: a = 25.333(3) Å, b = 6.299(1) Å, c = 15.161(3) Å,  $\beta = 90.93(3)^{\circ}$  and V = 2419.0(2) Å<sup>3</sup>. Ferraioloite has a heteropolyhedral layer structure with layers parallel to (100) and with isolated Mg(H<sub>2</sub>O)<sub>6</sub> octahedra and water molecules packing between the layers. The heteropolyhedral slabs have the same topology as falsterite, with Mn<sup>2+</sup> replacing Ca<sup>2+</sup> and with Al<sup>3+</sup> substituting for Fe<sup>3+</sup>.

Key-words: ferraioloite; new mineral; falsterite; pegmatite; Foote Lithium Company mine; crystal structure; synchrotron; phosphate.

#### 1. Introduction

The new mineral ferraioloite was discovered by one of the authors (JBS) in 2005 on the East dump of the Foote Lithium Company mine, Kings Mountain district, Cleveland County, North Carolina, USA (35°12'40''N, 81°21'20''W). The pegmatite exploited by the Foote Lithium Company mine is the type locality for twelve other minerals (*e.g.* White, 1981; Atencio *et al.*, 2008), seven of which are secondary phosphates.

The resemblance of the new phase to the recently described mineral falsterite (Kampf *et al.*, 2012) was noted early in our study; however, the very thin, curved nature of crystal plates presented challenges in its characterization, especially with respect to the determination of its crystal structure. Falsterite was described from the Palermo No. 1 pegmatite, North Groton, New Hampshire, USA, where it occurs in a secondary phosphate assemblage rather similar to that in which ferraioloite was discovered at the Foote mine. Falsterite has also been found at the

Estes pegmatite quarry, Baldwin, Maine, USA. At both of these occurrences, falsterite is associated with schoonerite (Kampf, 1977; Moore & Kampf, 1977), a mineral with which it has structural affinities. Interestingly, schoonerite has also been found in the same general assemblage as ferraioloite at the Foote mine. Considering that schoonerite is known from several other pegmatites, including the Hagendorf Süd pegmatite, Bavaria, Germany, it is reasonable to expect ferraioloite to be found in other phosphatebearing pegmatites in the future.

The species is named in honour of the late James (Jim) Anthony Ferraiolo (May 14, 1947–February 6, 2014). The mineral is pronounced /fe..(r) i: 'Ou IOu ait/ (/feə- i: 'o- loa-t/). Jim worked as scientific assistant at the American Museum of Natural History (AMNH) from April 1978 until August 1982 and also as transaction coordinator at the Smithsonian Institution's Museum of Natural History from September 1982 until April 1985. He was best known for his publication *A Systematic Classification of Nonsilicate Minerals* (Bulletin 172 of the AMNH, 1982), which was widely used in Museum collections, as a basis for collection classification and organisation (*e.g.* Museum Victoria, Australia). Recently, Jim was a member of the IMA CNMNC subcommittee for mineral group nomenclature and the subcommittee on unnamed minerals. Jim also spent more than a decade as a manager with mindat.org and was instrumental in publishing the description of ferro-laueite (Ferraiolo, 2012; Segeler *et al.*, 2012).

The mineral and name (IMA2015–066) were approved by the IMA CNMNC prior to publication. Two cotype specimens are housed in the collections of Museum Victoria, specimen M53492 and M53493, and two cotype specimens are deposited in the collections of the Natural History Museum of Los Angeles County, catalogue numbers 65593 and 65594.

## 2. Occurrence, location and physical and optical properties

The new mineral occurs in very small vughs contained in a thin seam of very fine-grained, sugary pegmatite ( $\sim 30 \times 10 \times 20$  cm) as a stringer in more typical pegmatite that was part of a large zinc-bearing boulder found on the East dump (the only zinc-bearing phosphates ever found at the locality were found in this boulder). Mn-bearing fluorapatite, sphalerite, muscovite and pyrite are common accessory minerals in the stringer as well as in other places in the larger boulder. Associated secondary minerals in order of abundance are: vivianite, fairfieldite/messelite (as boxwork-like networks forming cavity walls), phosphophyllite, scholzite/parascholzite, rittmannite, mangangordonite, kingsmountite, kastningite and, on two specimens, metaswitzerite.

Ferraioloite crystals occur as very thin greenish grey to lemon yellow plates or blades up to about 0.2 mm in length, but no more than a few  $\mu$ m thick (Fig. 1). Individual crystals may also show curved faces. The main faces observed are {010}, {100} and {011} (Fig. 2). The plates often form books or rosettes up to about 0.4 mm across. Crystals are transparent with a vitreous lustre, flexible with an irregular fracture, and have perfect cleavage on {100}. The Mohs' hardness is estimated to be about 2, based upon behaviour when broken.

The density could not be measured because insufficient material is available for direct measurement. The calculated density is 2.59 g cm<sup>-3</sup>, based on the empirical formula and single-crystal unit cell. Optically, ferraioloite crystals are biaxial (–), with indices of refraction  $\alpha = 1.575(\text{calc})$ ,  $\beta = 1.5825(5)$ ,  $\gamma = 1.5835(5)$ ,  $2V(\text{meas.}) = 40(5)^{\circ}$  and  $2V(\text{calc.}) = 40^{\circ}$ , measured in white light. The thinness of the plates made it impossible to accurately measure  $\alpha$ ; consequently, it has been calculated based upon  $\beta$ ,  $\gamma$  and 2V. Dispersion is weak: r > v, the orientation is:  $X \approx \mathbf{a}$ ,  $Y = \mathbf{b}$ ,  $Z \approx \mathbf{c}$  and pleochroism: X, Z = colourless, Y = blue grey;  $Y >> X \approx Z$ . The Gladstone–Dale compatibility is -0.0416 (good) using the empirical formula and single-crystal unit cell.



Fig. 1. Scanning electron microscope (SEM) image of intergrown blades of ferraioloite.



Fig. 2. Crystal drawing of a blade of ferraioloite.

#### 3. Chemical composition

Quantitative chemical analyses (10) of ferraioloite were carried out using a wavelength dispersive spectrometer on a JEOL JXA 8500F Hyperprobe operated at an accelerating voltage of 12 kV and a beam current of 3 nA. The beam was defocused to 5  $\mu$ m. Water could not be analysed directly because of the minute amount of sample available. H<sub>2</sub>O was calculated on the basis of P = 8, charge balance and 56 O atoms per formula unit (*apfu*), as determined by the crystal-structure analysis (see below). Analytical data are given in Table 1.

The empirical formula of ferraioloite (based on 8 P and 56 O *apfu*) is  $Ca_{0.21}Mg_{0.50}Mn^{2+}_{4.16}Fe^{2+}_{2.05}Al^{3+}_{2.01}Zn_{4.27}P_{8.00}H_{43.59}O_{56}$ . The simplified formula is  $MgMn^{2+}_{4.16}$ 

Const.	Mean	Range	SD	Standard
CaO	0.65	0.51-0.75	0.09	wollastonite (CaSiO <sub>3</sub> )
MgO	1.09	0.92-1.23	0.09	spinel (MgAl <sub>2</sub> O <sub>4</sub> )
MnO	16.05	14.2-19.51	1.36	rhodonite (MnSiO <sub>3</sub> )
ZnO	18.90	16.76-20.15	1.07	phosphophyllite (Zn <sub>2</sub> (Fe,Mn)(PO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O)
FeO	8.02	5.71-9.47	1.26	hematite ( $Fe_2O_3$ )
$Al_2O_3$	5.58	5.23-5.99	0.23	berlinite $(AlPO_4)$
$P_2O_5$	30.90	29.52-32.17	0.83	berlinite $(AIPO_4)$
H <sub>2</sub> O*	21.30			чт <i>у</i>
Total	102.49			

Table 1. Analytical results (wt.%) for ferraioloite.

\* Calculated from structure

 $(Fe^{2+}_{0.5}AI^{3+}_{0.5})_4Zn_4(PO_4)_8(OH)_4(H_2O)_{20}$ , which requires MgO 2.17, MnO 15.26, FeO 7.73, ZnO 17.52, Al<sub>2</sub>O<sub>3</sub> 5.48, P<sub>2</sub>O<sub>5</sub> 30.54, H<sub>2</sub>O 21.30, total 100.00 wt.%.

#### 4. Powder X-ray diffraction

Powder X-ray diffraction data for ferraioloite were obtained on a Rigaku R-Axis Rapid II curved–imaging– plate microdiffractometer utilising monochromatised MoK $\alpha$  radiation. A Gandolfi-like motion on the  $\varphi$  and  $\omega$ axes was used to randomize the sample. Observed *d* spacings and intensities were derived by profile fitting using JADE 2010 software (Materials Data Inc.). Data are given in Table 2. The unit-cell parameters refined from the powder data using JADE 2010 with whole-pattern fitting are: a = 25.320(6), b = 6.345(6), c = 15.267(6) Å,  $\beta = 91.031(5)^\circ$ , V = 2452.4(4) Å<sup>3</sup> and Z = 2, which are in excellent agreement with the single-crystal study below.

### 5. Single-crystal X-ray diffraction

A pale green 20  $\mu$ m  $\times$  10  $\mu$ m  $\times$  2  $\mu$ m lath of ferraioloite was mounted on a nylon loop, to minimise diffraction from the sample mount for an X-ray data collection on

Table 2. Powder X-ray data (d in Å) for ferraioloite (eight strongest lines in bold-face type).

I <sub>obs</sub>	$d_{\rm obs}$	$d_{\rm calc}$	Icalc	hkl	$I_{\rm obs}$	$d_{\rm obs}$	$d_{\rm calc}$	$I_{\rm calc}$	hkl	I <sub>obs</sub>	$d_{\rm obs}$	$d_{\rm calc}$ $I_{\rm calc}$	hkl
		13.1016	2.5	$\bar{1} 0 1$			2.8308	0.1	222			1.9574 0.2	<b></b> 417
		12.9155	2.4	101			2.8200	0.1	420			1.9365 0.1	13 0 1
100	12.7	12.6648	100.0	200			2.7882	0.1	$\bar{8} 1 1$			1.9335 0.2	824
1	7.58	7.5795	0.9	002			2.7737	0.2	811			1.9184 0.1	<u>2</u> 33
		6.1128	0.2	110	4	2.664	2.6604	0.4	$\overline{1} 2 3$	2	1.8942	1.9160 0.4	10 2 2
		5.8168	0.2	011			2.6557	0.4	123			1.9143 0.3	824
		5.2735	0.5	211			2.6492	1.0	$\bar{4} 2 2$			1.9043 0.5	10 2 2
1	4.95	4.9709	0.5	$\bar{1} 0 3$	3	2.616	2.6379	1.6	$\bar{5} 2 1$			1.8949 1.0	008
		4.9400	0.4	103			2.6302	1.5	521			1.8797 0.3	725
4	4.78	4.8284	0.3	$\bar{5} 0 1$			2.6203	0.6	$\bar{5} 0 5$			1.8785 0.2	$\overline{2} 0 8$
		4.7815	0.4	501	3	2.562	2.5831	0.7	505			1.8696 0.3	208
		4.7673	1.0	$\overline{1}$ 1 2			2.5545	0.9	<u>3</u> 23			1.8480 0.2	11 2 1
		4.7491	1.4	112			2.5419	0.5	323			1.8329 0.2	ī 3 4
1	4.33	4.3672	0.4	$\bar{3}$ 0 3			2.5244	0.6	620			1.8308 0.2	134
		4.3052	0.7	303			2.4838	0.2	<u>8</u> 13			1.8196 0.1	11 0 5
4	4.22	4.2216	1.1	600	3	2.404	2.4222	0.2	024			1.8012 0.1	13 1 2
		4.1832	0.8	312			2.4020	1.0	622			1.7628 0.1	732
		3.7771	0.2	<u>2</u> 13			2.3907	0.2	10 0 2			1.7598 0.2	10 24
		3.7500	0.1	213			2.3881	1.3	622			1.7506 0.2	327
3	3.699	3.7138	1.2	$\bar{6} 0 2$			2.3837	0.9	$\bar{2} 2 4$			1.7416 0.3	10 2 4
		3.6629	1.3	602	2	2.352	2.3746	0.3	224			1.7134 0.1	12 2 2
		3.6470	0.6	$\bar{2} 0 4$			2.3556	0.3	523			1.7033 0.1	1222
4	3.580	3.6146	0.4	$\frac{2}{2}04$			2.3427	0.4	$\bar{7}$ 0 5			1.6827 0.5	826
		3.6070	0.6	$\bar{5}03$			2.3382	0.1	116			1.6813 0.1	$\overline{15} 0 1$
		3.5489	0.9	503			2.3317	0.3	116			1.6753 0.2	15 0 1
		3.5326	0.2	$\bar{7} 0 1$			2.3276	0.3	$1\overline{0} \ 1 \ 1$			1.6637 0.4	826
5	3.499	3.5195	3.2	512			2.3171	0.4	10 1 1			1.6431 0.2	1404

$I_{\rm obs}$	$d_{\rm obs}$	$d_{\rm calc}$	$I_{\text{calc}}$	hkl	$I_{\rm obs}$	$d_{\rm obs}$	$d_{\rm calc}$	$I_{\text{calc}}$	hkl	$I_{\rm obs}$	$d_{\rm obs}$	$d_{\rm calc}$	$I_{\text{calc}}$	hkl
		3.5068	0.2	701			2.3056	0.2	705	2	1.6178	1.6237 0.	.2	028
		3.4832	2.9	512			2.1836	0.2	$\bar{6} 0 6$			1.6225 0.	.1 14	404
		3.4268	0.1	$\bar{6} 1 1$	2	2.153	2.1588	0.3	723			1.6133 0.	.1	$\bar{2} 2 8$
		3.4066	0.1	611			2.1526	0.5	606			1.6077 0.	.3 .	228
		3.3654	0.2	<b>4</b> 13			2.1486	0.8	$\bar{8} 2 2$			1.6046 0.	.1 1	$\overline{0} 1 7$
7	3.245	3.2754	1.0	$\bar{4}04$			2.1433	0.2	10 1 3			1.5996 0.	.1 1	$\overline{2} 2 4$
		3.2289	2.9	404			2.1403	0.2	516	3	1.5862	1.5940 0.	.2 1	125
		3.2153	0.7	114			2.1353	0.5	822			1.5832 0.	.3 1	224
		3.0623	0.1	$\bar{1} 2 1$	2	2.113	2.1187	0.3	10 1 3			1.5755 0.	.2 1	125
		3.0598	0.3	121			2.1159	0.2	516			1.5748 1.	.1 (	040
1	3.000	3.0161	0.4	$\overline{1}$ 0 5			2.1104	0.4	$\bar{6} 2 4$	2	1.5691	1.5688 0.	.2 14	420
		3.0046	0.3	105			2.1083	0.2	1103			1.5651 0.	.4 1	026
8	2.924	2.9648	0.8	$\bar{7}03$	2	2.083	2.0916	0.5	624			1.5627 0.	.4	240
		2.9386	1.0	$\bar{8} 0 2$			2.0903	0.1	1004			1.5460 0.	.4 10	026
		2.9196	0.2	703			2.0881	0.2	11 1 2			1.5226 0.	.1	ē 2 8
		2.9136	0.5	$\bar{7}$ 1 2			2.0822	0.8	<u>9</u> 21			1.5163 0.	.2	<u>9</u> 27
		2.9084	0.3	022			2.0754	0.5	921			1.4980 0.	.3	927
		2.9048	0.6	802			2.0714	0.2	11 1 2	2	1.4714	1.4702 0.	.1	ā 3 7
		2.8996	1.9	321			2.0266	0.1	$\bar{2}$ 1 7			1.4693 0.	.3 1	$\overline{6}04$
		2.8934	1.4	321			2.0168	0.1	217			1.4664 0.	.2	329
		2.8848	0.4	712			1.9906	0.3	$\bar{8}06$	2	1.4536	1.4625 0.	.2 1	325
5	2.869	2.8683	0.9	$\bar{3}$ 0 5			1.9815	0.1	716			1.4593 0.	.2 .2	329
		2.8630	0.4	613			1.9797	0.1	507			1.4568 0.	.2 1	<del>4</del> 2 4
		2.8388	1.1	305			1.9594	0.2	806			1.4524 0.	.2 1	604

Table 2. Continued

Table 3. Data collection and structure refinement details for ferraioloite.

Diffractometer X-ray radiation/power Temperature	ADSC Quantum 315r detector $\lambda = 0.7100 \text{ Å}$ 100 K
Structural formula	$\frac{\text{MgMn}^{2+}_{4}(\text{Fe}^{2+}_{0.5}\text{Al}^{3+}_{0.5})_{4}}{\text{Zn}_{4}(\text{PO}_{4})_{8}(\text{OH})_{4}(\text{H}_{2}\text{O})_{20}}$
Space group	I2/m
Unit-cell dimensions	a = 25.333(3) Å
	b = 6.299(1)  Å
	c = 15.161(3)  Å
	$\beta = 90.93(3)^{\circ}$
V	2419.0(2) Å <sup>3</sup>
Ζ	2
Absorption coefficient	$3.978 \text{ mm}^{-1}$
F(000)	1717
Crystal size	$20 \times 10 \times 2 \ \mu m$
θ range	1.55 to 30.52°
Index ranges	$-36 \le h \le 35, -7 \le k \le 7, \\ -21 < l < 21$
Reflections collected/unique	$17759/751$ [ $R_{int} = 0.1455$ ]
Reflections with $[I > 3\sigma(I)]$	565
Refinement method	Full-matrix least-squares on $F^2$
Parameters refined	98
Final <i>R</i> indices $[I > 3\sigma(I)]$	$R_{\rm obs} = 0.065, wR_{\rm obs} = 0.071$
<i>R</i> indices (all data)	$R_{\rm obs} = 0.092, w R_{\rm obs} = 0.0773$
Extinction coefficient	0.0006(11)
delta <i>F</i> , min, max	-0.70, 0.49

the micro-focus macromolecular beam line MX2 of the Australian Synchrotron. Data were collected at 100 K using an ADSC Quantum 315r detector and monochromatic radiation with a wavelength of 0.71086 Å. A  $\varphi$  scan was employed, with frame widths of  $1^{\circ}$  and a counting time per frame of 1 s. The data was integrated in P1 using XDS (Kabsch, 2010) and the absorption correction was carried out with SADABS (Bruker, 2001). The ultra-thin laths of ferraioloite gave relatively poor diffraction, with severe streaking of the diffraction spots and it was necessary to restrict the data used in the analysis to a resolution of 1 Å. Indexing of the synchrotron data gave a nearorthogonal body-centred cell with a = 25.333, b = 6.299, c = 15.161 Å,  $\alpha = 90.47$ ,  $\beta = 90.93$  and  $\gamma = 89.91^{\circ}$ . The departure of  $\alpha$  and  $\gamma$  from 90° was considered to be due to problems with centring on the streaked reflections. A structure solution was obtained in the monoclinic space group I2/m using SHELXT (Sheldrick, 2008, 2015). The close similarity of the heteropolyhedral layer model obtained to that for falsterite (Kampf et al., 2012) assisted in the assignment of cations to the different metal atom sites. As the refinement progressed, it became evident from site occupancies and bond distances that the Ca site in falsterite was replaced by Mn and the Fe sites, which contain  $0.5Fe^{2+}+0.5Fe^{3+}$  in falsterite, have the  $Fe^{3+}$  replaced by  $Al^{3+}$  in ferraioloite. The structure was refined using JANA2006 (Petříček & Dušek, 2006).

1325

1.4456 0.1

	x	у	Z	$U_{ m iso}$	Occ.	Bond valence
Heteropolyhedra	l layer atoms					
Zn	0.3138(7)	0.7478(2)	0.5013(1)	0.0408(8)	1	2.15
Mn1	0.1678(1)	0.5	0.6201(2)	0.042(1)	1	1.59
Mn2	0.1667(1)	0	0.3754(2)	0.044(1)	1	1.76
Fe1	0.25	0.25	0.75	0.042(2)	0.66(2)	2.65
Al1	0.25	0.25	0.75	0.042(2)	0.34(2)	
Fe2	0.75	0.25	0.75	0.053(2)	0.46(3)	2.59
Al2	0.75	0.25	0.75	0.053(2)	0.54(3)	
P1	0.2201(2)	0.5	0.4276(3)	0.042(2)	1	5.00
P2	0.3519(2)	0	0.3405(3)	0.036(1)	1	4.84
P3	0.2212(2)	0	0.5766(3)	0.033(1)	1	5.01
P4	0.3512(2)	0.5	0.6655(4)	0.046(2)	1	4.90
01	0.2204(3)	0.3096(11)	0.3655(5)	0.026(2)	1	1.77
O2	0.2709(3)	0.5	0.4868(5)	0.005(2)	1	2.33
O3	0.1703(4)	0.5	0.4836(9)	0.053(4)	1	1.71
O4	0.3886(5)	0	0.2608(7)	0.046(4)	1	1.25
05	0.2958(4)	0	0.2987(8)	0.025(3)	1	1.60
O6	0.3580(3)	0.1957(11)	0.4021(5)	0.028(2)	1	1.74
O7	0.2205(3)	0.2034(12)	0.6310(5)	0.031(2)	1	1.92
O8	0.2691(5)	0	0.5149(9)	0.057(4)	1	2.22
09	0.1746(7)	0	0.510(1)	0.120(8)	1	1.69
O10	0.3587(3)	0.6956(11)	0.6062(5)	0.030(2)	1	1.73
011	0.3944(4)	0.5	0.7387(6)	0.020(3)	1	1.22
O12	0.2977(5)	0.5	0.7129(10)	0.062(5)	1	1.79
O13 (OH)	0.2961(5)	0	0.7378(9)	0.036(3)	1	0.95
O14 (OH)	0.2018(10)	0	0.249(2)	0.109(7)	1	0.86
O15 (H <sub>2</sub> O)	0.1018(6)	0.754(2)	0.390(1)	0.092(5)	1	0.25
O16 (H <sub>2</sub> O)	0.0934(7)	0.289(3)	0.636(1)	0.102(5)	1	0.23
Interlayer atoms						
Mg	0.5	0.5	0.5	0.056(3)	1	2.66
Ow1*	0.505(1)	0	0.327(2)	0.119(8)	1	0.1
Ow2	0.5629(5)	0.5	0.5975(8)	0.034(3)	1	0.29
Ow3	0.5113(9)	0.5	0.749(2)	0.101(7)	1	0.1
Ow4	0.5279(7)	0.746(2)	0.440(1)	0.103(5)	1	0.52
Ow5	0.5	0.252(5)	0	0.16(1)	1	0.1

Table 4. Atom fractional coordinates, isotropic displacement parameters ( $\mathring{A}^2$ ) and site occupancies for ferraioloite.

\*Ow = interlayer water molecules

Refinement employing isotropic displacement parameters converged at  $R_{obs} = 0.07$  for 751 reflections at a resolution of 1.0 Å. Details of the data collection and structure refinement are provided in Table 3. Fractional coordinates, site occupancies and isotropic atom displacement parameters are given in Table 4. Included in Table 4 are bond valences calculated in JANA2006. Selected bond distances are reported in Table 5.

#### 6. Discussion of structure

The structure of ferraioloite is shown in projection along [010] in Fig. 3a. It is a heteropolyhedral layer structure with layers parallel to (100) and with isolated Mg(H<sub>2</sub>O)<sub>6</sub> octahedra and water molecules packing between the layers. The heteropolyhedral slabs have the same topology as those in the mineral falsterite,  $Ca_2MgMn^{2+}_{2}(Fe^{2+}_{0.5})$ 

Fe<sup>3+</sup><sub>0.5</sub>)<sub>4</sub>Zn<sub>4</sub>(PO<sub>4</sub>)<sub>8</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>14</sub> (Kampf *et al.*, 2012), shown in Fig. 3b, with Mn<sup>2+</sup> replacing Ca<sup>2+</sup> and with Al<sup>3+</sup> substituting for Fe<sup>3+</sup>. In falsterite, the slabs are bridged by edge-sharing dimers of MgO<sub>6</sub> octahedra which share edges with ZnO<sub>4</sub> tetrahedra in adjacent slabs. The Mg sites are half occupied in falsterite. In contrast, ferraioloite has isolated, fully occupied Mg(H<sub>2</sub>O)<sub>6</sub> octahedra between the slabs, and cohesion is maintained by hydrogen bonding between the water molecules and oxygen acceptors in the slabs as shown by the dashed lines in Fig. 3a. The replacement of the bridging dimeric units with H-bonded Mg(H<sub>2</sub>O)<sub>6</sub> octahedra results in a large (19%) expansion of the axis, normal to the layers, from 21.3 Å in falsterite to 25.3 Å in ferraioloite.

The H atoms were not located in the structure refinement, but the assignment of  $OH^2$  and  $H_2O$  can be inferred from bond-valence calculations, the results of which are

(a) Zn O10 1.967(9) Fe2 01 1.953(8) 1.913(5) 01 1.953(8) Ow3 O2 08 1.963(7) 05 2.084(6) 06 1.923(8) 05 2.084(6)Ow2 bw1 <Zn-O> 1.942 014 1.99(2) Mg 014 1.99(2) Mn1 013 2.333(14) <Fe-O> 2.009 O 2.308(8) 07 07 2.308(8) P1 01 1.525(8) O3 2.072(13)01 1.525(8) 016 2.311(17) 02 1.556(9) 016 03 1.533(13) 2.311(17) <Mn-O> 2.273 <P-O> 1.535 Mn2 01 2.384(8)P2 04 1.536(13) 1.547(11) 01 2.384(8) 05 (b) 014 2.10(3) 06 1.553(8) 014 2.04(2)06 1.553(8) 015 <P-O> 1.547 2.27(1)015 2.27(1)<Mn-0> 2.241 P3 07 1.524(8)07 1.524(8) 2.156(12) 1.544(14) Mg Ow2 08 Ow2 2.156(12) 09 1.54(2) Ow4 1.934(15)<P-O> 1.533 Mn Ow4 1.934(15)P4 Ow4 1.934(15)O10 1.538(8) Ow4 1.934(15) O10 1.538(8) Mg 2.008 1.544(10) <Mg-O> 011 012 1.545(13) Fe1 013 1.971(8) <P-O> 1.541 O13 1.971(8) 07 1.965(8) b 07 1.965(8) 012 2.068(8) 012 2.068(8) <Fe-O> 2.001

Table 5. Selected bond distances (Å) in ferraioloite.

Fig. 3. (a) Crystal structure of ferraioloite. Dashed lines correspond to hydrogen bonds between interlayer water molecules and layer oxygen atoms. (b) Crystal structure of falsterite. (online version in colour)

Table 6. Comparative data for ferraioloite and falsterite.

	Ferraioloite	Falsterite
Formula	$MgMn^{2+}_{4}(Fe^{2+}_{0.5}Al^{3+}_{0.5})_{4}Zn_{4}(PO_{4})_{8}(OH)_{4}(H_{2}O)_{20}$	Ca2MgMn <sup>2+</sup> 2(Fe <sup>2+</sup> 0.5Fe <sup>3+</sup> 0.5)4Zn4(PO4)8(OH)4(H2O)14
Symmetry	Monoclinic, I2/m	Monoclinic, $P2_1/c$
Cell	a = 25.333(3) Å, $b = 6.299(1)$ Å,	a = 6.387(2) Å, $b = 21.260(7)$ Å, $c = 15.365(5)$ Å,
	$c = 15.161(3) \text{ Å}, \beta = 90.93(3)^{\circ}$	$\beta = 90.564(6)^{\circ}$
	$V = 2419.0(2) \text{ Å}^3$	$V = 2086.2(1.1) \text{ Å}^3$
Ζ	2	2
Strongest powder-pattern	12.7, 100 (200)	12.86, 34 (011)
lines d, I, hkl	4.78, 4 (112)	10.675, 100 (020)
	3.499, 5 (512)	4.043, 18 (132)
	3.245, 7 (404)	3.220, 25 (152)
	2.924, 8 (321)	3.107, 14 (044)
	2.869, 5 (305)	2.846, 19 (222)
Optics	Biaxial (–)	Biaxial (-)
	$\alpha = 1.575$ (calc), $\beta = 1.5825(5)$ , $\gamma = 1.5835(5)$	$\alpha = 1.575(10), \beta = 1.600(5), \gamma = 1.610(5)$
	$2V(\text{meas.}) = 40(5)^{\circ}; 2V(\text{calc.}) = 40^{\circ}$	$2V(\text{meas.}) = 60(10)^{\circ}; 2V(\text{calc.}) = 63.8^{\circ}$
	Pleochroism: $X, Z =$ colourless,	Pleochroism: $X, Z =$ colourless to very pale yellow,
	$Y =$ blue grey; $Y >> X \approx Z$	$Y =$ blue green; $Y >> X \approx Z$
	Orientation: $X \approx \mathbf{a}, Y = \mathbf{b}, Z \approx \mathbf{c}$	Orientation: $X \approx \mathbf{b}$ , $Y = \mathbf{a}$ , $Z \approx \mathbf{c}$

given in Table 4. These show that the anions forming shared edges between the Mn-centred and Fe-centred octahedra, O13 and O14, are hydroxyl ions, and the unshared vertices of the Mn-centred octahedra, O15 and O16, are water molecules. The unshared vertices O4 and O11 of the P2- and P4-centred tetrahedra have low valence sums, 1.25 and 1.22, respectively. The valence requirements for these oxygen atoms are met by H-bonding as shown in Fig. 3a. The sites Fe1 and Fe2 contain a mixture of Al and Fe, and the valence sums for these sites, 2.65 and 2.59, respectively, are consistent with the Fe being predominantly in the divalent state. This compares with falsterite, where these two sites contain an equal mixture of  $Fe^{2+}$  and  $Fe^{3+}$ . Ferraioloite is closely related to falsterite, both structurally and chemically. A comparison of the properties of the two minerals is given in Table 6.

The pleochroic colours exhibited by ferraioloite and falsterite deserve additional comment. Both minerals exhibit distinct colour only along their 6-Å axis, **b** in ferraioloite and **a** in falsterite. This is the direction of edge-sharing chains of Fe1 and Fe2 octahedra in each structure. Falsterite exhibits a strong blue-green colour in this direction, while ferraioloite exhibits a distinctly less intense blue-grey colour. Kampf *et al.* (2012) attributed the colour in falsterite to the strong absorption typical of Fe<sup>2+</sup>-Fe<sup>3+</sup> charge transfer. It seems likely that the blue-grey colour observed for ferraioloite is also due to Fe<sup>2+</sup>-Fe<sup>3+</sup> charge transfer along this chain and that it is much weaker because only a very small portion of the Fe is trivalent and the presence of Al<sup>3+</sup> effectively "dilutes" the effect of the charge transfer.

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