

1 Revision 1

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3 Nizamoffite,  $\text{Mn}^{2+}\text{Zn}_2(\text{PO}_4)_2(\text{H}_2\text{O})_4$ , the Mn analogue of hopeite from the Palermo No. 1

4 pegmatite, North Groton, New Hampshire.

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16

17 **Abstract**

18 Nizamoffite, ideally  $\text{Mn}^{2+}\text{Zn}_2(\text{PO}_4)_2(\text{H}_2\text{O})_4$ , is a new mineral from the Palermo No.1

19 pegmatite in North Groton, Grafton County, New Hampshire, U.S.A. It formed as the result

20 of secondary alteration of primary triphylite and associated sphalerite. The crystals occur as

21 colorless prisms up to 1 mm in length and 0.5 mm in diameter. The prisms are elongated and

22 lightly striated parallel to [001] and exhibit the forms {100}, {010}, {230}, {011}, {031}, and

23 {111}. The mineral is transparent and has a white streak, vitreous luster, Mohs hardness of

24 about 3½, brittle tenacity, irregular fracture, and three cleavages: perfect on {010}, good on

25 {100}, and fair on {001}. The measured and calculated densities are 3.00(1) and 2.961 g/cm<sup>3</sup>,

26 respectively. It is optically biaxial (-),  $\alpha = 1.580(1)$ ,  $\beta = 1.590(1)$ ,  $\gamma = 1.591(1)$  (white light),  
27  $2V_{\text{meas}} = 28(1)^\circ$  and  $2V_{\text{calc}} = 35^\circ$ . Nizamoffite exhibits strong dispersion,  $r < v$ . The optical  
28 orientation is  $X = \mathbf{a}$ ,  $Y = \mathbf{c}$ ,  $Z = \mathbf{b}$  and the mineral is nonpleochroic. Electron-microprobe  
29 analyses (average of 10), with H<sub>2</sub>O calculated on structural grounds, provided: CaO 0.20,  
30 MgO 0.61, MnO 15.80, ZnO 33.34, Fe<sub>2</sub>O<sub>3</sub> 2.81, Al<sub>2</sub>O<sub>3</sub> 0.10, P<sub>2</sub>O<sub>5</sub> 32.05, H<sub>2</sub>O 15.95, total  
31 100.23 wt%. The empirical formula (based on 12 O atoms) is:  
32  $(\text{Mn}^{2+}_{0.99}\text{Ca}_{0.02})_{\Sigma 1.01}(\text{Zn}_{1.82}\text{Fe}^{3+}_{0.12}\text{Mg}_{0.07})_{\Sigma 2.01}(\text{P}_{1.00}\text{O}_4)_2(\text{H}_{1.96}\text{O})_4$ . The mineral dissolves readily  
33 in cold, dilute HCl. Nizamoffite is orthorhombic, *Pnma*, with the unit-cell parameters:  $a =$   
34  $10.6530(4)$ ,  $b = 18.4781(13)$ ,  $c = 5.05845(15)$  Å,  $V = 995.74(8)$  Å<sup>3</sup>, and  $Z = 4$ . The eight  
35 strongest lines in the X-ray powder diffraction pattern are [ $d_{\text{obs}}$  in Å( $I$ )( $hkl$ )]: 9.27(71)(020);  
36 4.62(37)(040,220); 4.43(24)(111); 3.424(52)(240,221); 2.873(100)(241); 2.644(36)(400,331);  
37 2.540(33)(420,161,002); and 1.953(36)(281). Nizamoffite is isostructural with hopeite. The  
38 structure ( $R_1 = 1.7\%$  for 1014  $F_o > 4\sigma F$ ) contains corner-sharing zigzag chains of ZnO<sub>4</sub>  
39 tetrahedra along [001]. The chains are connected by corner sharing with PO<sub>4</sub> tetrahedra to  
40 form sheets parallel to {010}. Three of the four PO<sub>4</sub> vertices link to ZnO<sub>4</sub> tetrahedra in the  
41 sheet, while the fourth links to an octahedron between the sheets. Each octahedron links to  
42 one tetrahedron from each of two adjacent sheets, thereby linking the sheets in the [010]  
43 direction. The octahedron contains Zn in hopeite and Mn in nizamoffite.

44  
45 Keywords: nizamoffite; new mineral; crystal structure; hopeite; secondary phosphate;  
46 Palermo No. 1 pegmatite, New Hampshire, U.S.A.

47

## 48 Introduction

49 The new mineral described herein was discovered at the Palermo No.1 pegmatite  
50 (Segeler et al. 1981; Whitmore and Lawrence 2004) in North Groton, Grafton County, New  
51 Hampshire, U.S.A. (43° 45.038'N 71° 53.378'W), by James Nizamoff and one of the authors

52 (RWW) in 2003. The Palermo No. 1 pegmatite is the type locality for eleven new phosphate  
53 species, not including the new mineral described herein: whitlockite (Fronzel 1941), wolfeite  
54 and xanthoxenite (Fronzel 1949), palermoite (Fronzel and Ito 1965), bjarebyite (Moore et al.  
55 1973), whitmoreite (Moore et al. 1974), foggite, goedkenite, and samuelsonite (Moore et al.  
56 1975), schoonerite (Moore and Kampf 1977), and falsterite (Kampf et al. 2012). The paper  
57 describing the last of these includes a synopsis of the mineralogy and geology of the deposit.

58         The new species is named nizamoffite in honor of James W. Nizamoff (b. 1971) in  
59 recognition of his research on pegmatite mineralogy in general, and especially on the  
60 phosphate mineralogy of the Palermo pegmatites at North Groton, New Hampshire. Mr.  
61 Nizamoff is one of the discoverers of the new mineral and provided the specimens used for its  
62 characterization. He is a co-author of the descriptions of the new minerals falsterite, galliskiite  
63 and zigrasite. He has agreed to the naming of the mineral in his honor. The new mineral and  
64 name have been approved by the Commission on New Minerals, Nomenclature, and  
65 Classification of the International Mineralogical Association (IMA 2012-076). Two cotype  
66 specimens are deposited in the Natural History Museum of Los Angeles County under  
67 catalogue numbers 64009 and 64010.

68

### 69 **Occurrence and paragenesis**

70 Nizamoffite was found in a Zn- and Pb-rich phosphate-carbonate assemblage (Nizamoff et al.  
71 2007) along the margin of a 1.5 m triphylite crystal in the core-margin of the Palermo No. 1  
72 pegmatite. The triphylite crystal is rimmed on one side by a 10 to 30 cm thick rind of siderite,  
73 fluorapatite, and quartz. This carbonate-rich zone also contains minor amounts of sulfide  
74 minerals including pyrite, sphalerite, galena, and chalcopyrite. A significant portion of the  
75 sulfides have been altered by aqueous solutions, resulting in the formation of numerous  
76 secondary Zn- and Pb-bearing phosphate and carbonate species. Nizamoffite is a relatively

77 late-formed phase occurring as well-formed crystals in vugs in direct association with  
78 childrenite-eosphorite, crandallite-goyazite, fairfieldite-messelite, falsterite, fluorapatite,  
79 frondelite-rockbridgeite, mitridatite, phosphophyllite, pyrite, quartz, siderite, schoonerite,  
80 sphalerite, and vivianite. Other secondary species observed in the assemblage include  
81 cerussite, keckite, parascholzite, pyromorphite, and smithsonite.

82 The redox conditions for this assemblage span the boundary between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$   
83 stability, as indicated by the presence of minerals containing  $\text{Fe}^{2+}$ , minerals containing  $\text{Fe}^{3+}$ ,  
84 and minerals containing both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . We have assumed all Fe in nizamoffite to be 3+  
85 because that is most consistent with its presence in the tetrahedral Zn site in the structure.  
86 Furthermore, the structural site occupancy calculations using the program OccQP (see below),  
87 indicate that all Fe in nizamoffite is 3+.

88

### 89 **Physical and optical properties**

90 Nizamoffite crystals occur as colorless prisms up to 1 mm in length and 0.5 mm in diameter.  
91 The mineral is orthorhombic holosymmetric (point group *mmm*). Prisms are elongated and  
92 lightly striated parallel to [001] and exhibit the forms {100}, {010}, {230}, {011}, {031}, and  
93 {111} (Fig. 1). Nizamoffite is colorless and has a white streak. Crystals are transparent and  
94 have vitreous luster. Nizamoffite does not fluoresce in long or short wave ultraviolet light.  
95 The Mohs hardness is about 3½, the tenacity is brittle, the fracture is irregular, and there are  
96 three cleavages: perfect on {010}, good on {100}, and fair on {001}. The density measured  
97 by sink-float in an aqueous solution of lithium metatungstate is 3.00(1). The calculated  
98 density based on the empirical formula and single crystal unit cell is 2.961 g/cm<sup>3</sup>. Nizamoffite  
99 dissolves readily in cold, dilute HCl.

100 Optically, nizamoffite is biaxial negative, with  $\alpha = 1.580(1)$ ,  $\beta = 1.590(1)$ ,  $\gamma =$   
101 1.591(1), measured in white light. The 2V, measured directly by conoscopic observation, is

102 28(1)°. The calculated  $2V$  is 35°. Nizamoffite exhibits strong dispersion,  $r < v$ . The optical  
103 orientation is  $X = \mathbf{a}$ ,  $Y = \mathbf{c}$ ,  $Z = \mathbf{b}$  and there is no pleochroism.

104

#### 105 **Chemical composition**

106 Ten chemical analyses were carried out using an ARL-SEMQ electron microprobe in the  
107 Department of Earth and Environmental Science, University of New Orleans (WDS mode, 15  
108 kV, 10 nA, and 2–3  $\mu\text{m}$  beam diameter). No other elements were detected by EDS. Other  
109 likely elements were sought by EMPA, but none were found to be above the limit of  
110 detection. Insufficient material is available for direct water determination. The  $\text{H}_2\text{O}$  content is  
111 calculated by stoichiometry based upon the structure determination. Analytical data and  
112 standards are given in Table 1.

113 The empirical formula (based on 12 O atoms) is

114  $(\text{Mn}^{2+}_{0.99}\text{Ca}_{0.02})_{\Sigma 1.01}(\text{Zn}_{1.82}\text{Fe}^{3+}_{0.12}\text{Mg}_{0.07})_{\Sigma 2.01}(\text{P}_{1.00}\text{O}_4)_2(\text{H}_{1.96}\text{O})_4$ . The simplified formula is  
115  $\text{MnZn}_2(\text{PO}_4)_2(\text{H}_2\text{O})_4$ , which requires MnO 15.84, ZnO 36.35,  $\text{P}_2\text{O}_5$  31.71,  $\text{H}_2\text{O}$  16.10, total  
116 100.00 wt%.

117 The Gladstone-Dale compatibility index  $1 - (K_p/K_c)$  as defined by Mandarino (1981)  
118 provides a measure of the consistency among the average index of refraction, calculated  
119 density, and chemical composition. For nizamoffite, the compatibility index is 0.033 based on  
120 the empirical formula, within the range of excellent compatibility.

121

#### 122 **X-ray crystallography and structure refinement**

123 Both powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid  
124 II curved imaging plate microdiffractometer, with monochromatized  $\text{MoK}\alpha$  radiation. For the  
125 powder-diffraction study, a Gandolfi-like motion on the  $\varphi$  and  $\omega$  axes was used to randomize  
126 the sample and observed  $d$ -spacings and intensities were derived by profile fitting using JADE

127 2010 software. The powder data are presented in Table 2. The orthorhombic (*Pnma*) unit-cell  
128 parameters refined from the powder data using whole pattern fitting are:  $a = 10.647(4)$ ,  $b =$   
129  $18.451(8)$ ,  $c = 5.047(2)$  Å, and  $V = 991.4(7)$  Å<sup>3</sup>.

130 The Rigaku CrystalClear software package was used for processing the structure data,  
131 including the application of an empirical multi-scan absorption correction using ABSCOR  
132 (Higashi 2001). The structure was solved by direct methods using SIR2004 (Burla et al.  
133 2005), after which the coordinates were transformed to conform with those reported for  
134 hopeite in most earlier reports (Hill and Jones, 1976; Haussühl *et al.*, 1991). SHELXL-97  
135 software (Sheldrick 2008) was used, with neutral atom scattering factors, for the refinement of  
136 the structure. The occupancies of the octahedral (Mn) and large tetrahedral (Zn) sites were  
137 calculated using the program OccQP (Wright et al. 2001), which uses quadratic equations in a  
138 constrained least-squares formulation to optimize occupancy assignments based upon site  
139 scattering, chemical composition, charge balance, bond valence and cation-anion bond  
140 lengths. The optimization indicates deficiencies at both cation sites and somewhat different  
141 distributions of cations compared with what we deem most likely and have provided in the  
142 empirical formula; however, both are consistent with the ideal formula  $\text{Mn}^{2+}\text{Zn}_2(\text{PO}_4)_2(\text{H}_2\text{O})_4$ .

143 The positions of H atoms in the three H<sub>2</sub>O groups, OW1, OW2, and OW3, were  
144 located in the difference-Fourier maps and were refined using soft O–H distance constraints  
145 of 0.82(5) Å and no H–H distance constraints. The isotropic displacement parameters for the  
146 H sites were fixed at 0.05 Å<sup>2</sup> and, because more than one configuration was indicated for two  
147 of the H<sub>2</sub>O groups (OW2 and OW3), the occupancies of the H sites were refined. One H site  
148 (H1) on a general position is associated with the OW1 site on a mirror plane. This site refined  
149 to nearly full occupancy. The OW2 site, also on the mirror plane, has two H sites associated  
150 with it. One (H2a) is on the mirror plane and refined to nearly full occupancy, while the  
151 second (H2b) is on a general position and refined to close to half occupancy. These H sites,

152 therefore, define two different configurations for the OW2 H<sub>2</sub>O group. The third H<sub>2</sub>O group  
153 (OW3) is on a general position has four H sites (H3a, H3b, H3c, and H3d) also on general  
154 positions associated with it. The H3a site refined to nearly full occupancy, while the H3b,  
155 H3c, and H3d site occupancies refined roughly to ½, ¼, and ¼, respectively. The OW3 H<sub>2</sub>O  
156 group, therefore, has three different configurations. In the final refinement, the occupancies of  
157 the H sites were fixed at full, ½, and ¼ occupancies, in accord with their refined occupancies.

158 The details of the data collection and the final structure refinement are provided in  
159 Table 3. The final fractional coordinates and atom displacement parameters are provided in  
160 Table 4. Selected interatomic distances are listed in Table 5 and bond valences in Table 6.

161

## 162 **Description of the structure**

163 Nizamoffite is isostructural with hopeite (Whitaker, 1975; Hill and Jones, 1976;  
164 Haussühl *et al.*, 1991). The structure contains corner-sharing zigzag chains of ZnO<sub>4</sub> tetrahedra  
165 along [001]. The chains are connected by corner sharing with PO<sub>4</sub> tetrahedra to form sheets  
166 parallel to {010} (Fig. 2). Three of the four PO<sub>4</sub> vertices link to ZnO<sub>4</sub> tetrahedra in the sheet,  
167 while the fourth links to an octahedron between the sheets. Each octahedron links to one  
168 tetrahedron from each of two adjacent sheets, thereby linking the sheets in the [010] direction  
169 (Fig. 3). The octahedron contains Zn in hopeite and Mn in nizamoffite. The dominance of Mn  
170 in the octahedral site in nizamoffite is confirmed by computations using the program OccQP,  
171 which optimizes site occupancies based upon site scattering, chemical composition, charge  
172 balance, bond valence and cation-anion bond lengths.

173 Synthetic hopeites, including those substituted with cations such as Mn<sup>2+</sup>, Ni<sup>2+</sup>, and  
174 Mg, have been studied extensively because of their technological applications, particularly  
175 with respect to corrosion resistant coatings on galvanized steel (*c.f.* Arnaud *et al.* 1988;  
176 Haussühl *et al.* 1991; Herschke *et al.* 2004; Schofield *et al.* 2007). In Nature, there are two

177 polymorphs of  $\text{Zn}_3(\text{PO}_4)_2 \cdot 4(\text{H}_2\text{O})$ , hopeite (orthorhombic) and parahopeite (triclinic). In  
178 laboratory studies, two orthorhombic polymorphs with somewhat different properties have  
179 been reported and have been designated  $\alpha$ -hopeite and  $\beta$ -hopeite. As noted by Herschke et al.  
180 (2004),  $\alpha$ -hopeite is considered more stable and  $\beta$ -hopeite forms at lower temperature (20°C),  
181 but the structures of the two polymorphs are apparently identical except for the orientation of  
182 the H atoms of one of the  $\text{H}_2\text{O}$  groups. The differing properties of  $\alpha$ -hopeite and  $\beta$ -hopeite  
183 have been attributed to the resultant difference in hydrogen bonding.

184         The locations of the H atoms and the configuration of the hydrogen bonds in  
185 nizamoffite are shown in Figure 4, and are compared to those determined for  $\alpha$ -hopeite and  $\beta$ -  
186 hopeite by Herschke et al. (2004). [It should be noted that Herschke et al. (2004) used a  
187 different space group setting (*Pbnm*) and atom numbering scheme, so our foregoing  
188 comments are based upon our scheme.] Herschke et al. (2004) showed that the configurations  
189 of the H atoms of the OW2 and OW3  $\text{H}_2\text{O}$  groups are essentially the same in the structures of  
190  $\alpha$ -hopeite and  $\beta$ -hopeite, while they differ for the OW1  $\text{H}_2\text{O}$  group. For  $\alpha$ -hopeite, the H  
191 atoms of the OW1 group correspond to a single site on a general position reflected across the  
192 mirror plane containing the OW1 site, while for  $\beta$ -hopeite, the H atoms of this group lie on  
193 the mirror plane [although Herschke et al. (2004) apparently located only one of these H atom  
194 sites]. As seen in Figure 4, the H atom positions and hydrogen bonds for nizamoffite most  
195 closely correspond with those in  $\alpha$ -hopeite. The only significant difference is the  $\frac{1}{4}$ -occupied  
196 H3c and H3d sites. The H3c atoms form hydrogen bonds to adjacent OW3 atoms in the same  
197 octahedral coordination. The H3d atoms form hydrogen bonds to an OW2 atom in a different  
198 octahedral coordination.

199

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204

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242 Goedkenite,  $(\text{Sr,Ca})_2\text{Al}(\text{OH})[\text{PO}_4]_2$ ; and Samuelsonite,  
243  $(\text{CaBa})\text{Fe}^{2+}\text{Mn}^{2+}\text{Ca}_8\text{Al}_2(\text{OH})_2[\text{PO}_4]_{10}$ : Three new species from the Palermo No. 1  
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- 262
- 263

## FIGURE CAPTIONS

264

265

266 Figure 1. Crystal drawing of nizamoffite; clinographic projection in standard orientation.

267

268 Figure 2. The sheet of corner-sharing  $\text{ZnO}_4$  and  $\text{PO}_4$  tetrahedra in the structure of nizamoffite  
269 viewed down **b**. Oxygen atoms are labeled with numbers.

270

271 Figure 3. The structure of nizamoffite viewed down **c**. Oxygen atoms are labeled with  
272 numbers.

273

274 Figure 4. Hydrogen bonding in nizamoffite, hopeite- $\alpha$ , and hopeite- $\beta$ . Hydrogen bonds are  
275 shown as thin black lines. The gray spheres are the octahedrally coordinated cations and the  
276 bonds to the O atoms surrounding them are shown as sticks. Oxygen atoms in the nizamoffite  
277 structure are labeled with numbers and H atoms with letters as appropriate.

278

279 Table 1. Analytical results for nizamoffite (average of 10 analyses).  
280

Constituent	wt%	Range	SD	Standard
CaO	0.20	0.18–0.23	0.02	Fluorapatite ( $K\alpha$ )
MgO	0.61	0.45–0.71	0.08	Triphylite ( $K\alpha$ )
MnO	15.80	15.55–15.91	0.10	Lithiophilite ( $K\alpha$ )
ZnO	33.34	33.01–33.66	0.22	ZnO ( $K\alpha$ )
Al <sub>2</sub> O <sub>3</sub>	0.10	0.07–0.12	0.02	Amblygonite ( $K\alpha$ )
Fe <sub>2</sub> O <sub>3</sub>	2.18	1.90–2.33	0.15	Triphylite ( $K\alpha$ )
P <sub>2</sub> O <sub>5</sub>	32.05	31.88–32.30	0.13	Triphylite ( $K\alpha$ )
H <sub>2</sub> O*	15.95			
Total	100.23			

\* Calculated from the structure

281  
282

283 Table 2. Powder X-ray data for nizamoffite.  
 284

$I_{obs}$	$d_{obs}$	$d_{calc}$	$I_{calc}$	$hkl$	$I_{obs}$	$d_{obs}$	$d_{calc}$	$I_{calc}$	$hkl$
71	9.27(8)	9.2389	89	020	4	1.794(19)	1.7915	2	291
8	5.35(14)	5.3265	10	200	7	1.741(12)	1.7449	2	480
12	5.14(10)	5.1181	17	210			1.7436	4	620
21	4.88(5)	4.8788	19	011			1.7340	2	551
37	4.62(3)	{ 4.6195 4.6145	{ 38 4	{ 040 220	12	1.704(9)	{ 1.7055 1.7045	{ 2 6	{ 082 442
24	4.43(4)	4.4358	21	111	11	1.677(11)	1.6841	6	182
		4.0958	4	121			1.6769	3	391
19	4.05(4)	4.0289	19	230	13	1.647(7)	1.6654	2	103
14	3.91(4)	3.9090	15	031			1.6502	3	2·10·1
7	3.67(6)	{ 3.6698 3.6679	{ 3 4	{ 131 201	8	1.611(9)	1.6495	3	481
		3.4898	23	240			1.6484	3	621
52	3.424(13)	{ 3.4091 3.4091	{ 40 40	{ 221 221	17	1.538(6)	1.6390	2	123
5	3.15(5)	3.1514	6	231			1.6263	3	033
5	3.01(5)	{ 3.0363 2.9840	{ 3 6	{ 250 051	18	1.576(5)	1.6047	5	522
100	2.873(8)	2.8725	100	241	18	1.576(5)	1.5749	12	641
36	2.644(9)	{ 2.6661 2.6633	{ 4 19	{ 260 400	7	1.490(12)	1.5382	9	0·12·0
		2.6284	22	331			1.5182	15	243
33	2.540(8)	{ 2.5590 2.5538	{ 14 5	{ 420 161	8	1.465(11)	1.4920	4	0·10·2
		2.5292	17	002			1.4716	3	661
17	2.440(11)	2.4394	12	022	13	1.444(7)	1.4649	2	163
10	2.357(16)	2.3585	9	261			1.4541	4	4·10·1
22	2.286(8)	2.3097	5	080	14	1.423(6)	1.4465	2	343
		{ 2.2857 2.2851	{ 5 4	{ 171 132			1.4403	2	562
		2.2835	6	421			1.4363	5	482
		{ 2.2184 2.2179	{ 2 4	{ 042 222			1.4250	4	263
8	2.215(19)	{ 2.2010 2.2010	{ 2 2	{ 431 431	10	1.361(6)	1.4204	2	413
9	2.170(17)	2.1718	7	142	10	1.361(6)	1.4198	2	2·12·1
12	2.116(11)	{ 2.2835 2.2184	{ 6 2	{ 421 042	4	1.382(13)	1.3862	3	642
		2.2179	4	222			1.3653	5	363
9	2.170(17)	2.1718	7	142	5	1.332(13)	1.3561	4	681
12	2.116(11)	{ 2.2010 2.1191	{ 2 3	{ 431 280	8	1.316(11)	1.3330	3	4·12·0
		2.1137	8	361			1.3194	4	283
18	2.013(7)	{ 2.1191 2.0145	{ 3 9	{ 280 460	4	1.301(16)	1.3152	2	0·12·2
		2.0107	8	322			1.3142	2	662
36	1.953(5)	1.9545	30	281	7	1.277(6)	1.3017	2	4·10·2
22	1.834(6)	{ 2.0107 1.8349	{ 8 5	{ 322 262	10	1.241(4)	1.2754	4	821
		1.8340	14	402			1.2443	4	124
		1.8340	14	402			1.2419	4	2·14·1

Note: Only calculated lines with intensities greater than 2 are shown unless they correspond to observed lines.

285 Table 3. Data collection and structure refinement details for nizamoffite.  
 286

287	Diffractionmeter	Rigaku R-Axis Rapid II
288	X-ray radiation / power	MoK $\alpha$ ( $\lambda = 0.71075 \text{ \AA}$ )
289	Temperature	298(2) K
290	Structural formula*	(Mn <sup>2+</sup> <sub>0.819</sub> Fe <sup>3+</sup> <sub>0.080</sub> Mg <sub>0.063</sub> Al <sub>0.008</sub> Ca <sub>0.004</sub> ) $\Sigma$ 0.974
291		(Zn <sub>1.796</sub> Mn <sub>0.154</sub> Fe <sup>3+</sup> <sub>0.033</sub> ) $\Sigma$ 1.983(PO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>
292	Space group	<i>Pnma</i>
293	Unit cell dimensions	<i>a</i> = 10.6530(4) $\text{\AA}$
294		<i>b</i> = 18.4781(13) $\text{\AA}$
295		<i>c</i> = 5.05845(15) $\text{\AA}$
296	<i>V</i>	995.74(8) $\text{\AA}^3$
297	<i>Z</i>	4
298	Density (for above formula)	2.940 g cm <sup>-3</sup>
299	Absorption coefficient	6.058 mm <sup>-1</sup>
300	<i>F</i> (000)	863.8
301	Crystal size	110 x 45 x 25 $\mu\text{m}$
302	$\theta$ range	3.83 to 27.47°
303	Index ranges	$-13 \leq h \leq 13, -23 \leq k \leq 23, -4 \leq l \leq 6$
304	Reflections collected/unique	5260/1160 [ <i>R</i> <sub>int</sub> = 0.023]
305	Reflections with <i>F</i> <sub>o</sub> > 4 $\sigma$ <i>F</i>	1014
306	Completeness to $\theta = 27.47^\circ$	98.8%
307	Max. and min. transmission	0.863 and 0.556
308	Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
309	Parameters refined	102
310	GoF	1.072
311	Final <i>R</i> indices [ <i>F</i> <sub>o</sub> > 4 $\sigma$ ( <i>F</i> )]	<i>R</i> <sub>1</sub> = 0.017, w <i>R</i> <sub>2</sub> = 0.037
312	<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.022, w <i>R</i> <sub>2</sub> = 0.038
313	Largest diff. peak/hole	+0.32/-0.35 e $\text{\AA}^{-3}$
314		
315	<i>Notes:</i> <i>R</i> <sub>int</sub> = $\Sigma F_o^2 - F_o^2(\text{mean}) /\Sigma[F_o^2]$ . GoF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ . <i>R</i> <sub>1</sub> = $\Sigma F_o  -$	
316	$ F_c /\Sigma F_o $ . w <i>R</i> <sub>2</sub> = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ . <i>w</i> = $1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where <i>a</i> is	
317	0.0177, <i>b</i> is 0.4086 and <i>P</i> is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$ .	
318	* Site occupancies calculated using the program OccQP (Wright et al. 2001).	

319 Table 4. Fractional coordinates and atom displacement parameters ( $\text{\AA}^2$ ) for nizamoffite.

320		$x/a$	$y/b$	$z/c$	$U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
321	Mn*	0.25984(3)	1/4	0.06749(8)	0.01561(10)	0.01387(19)	0.0193(2)	0.0136(2)	0.000	-0.00115(16)	0.000
322	Zn*	0.143185(19)	0.499051(11)	0.20876(4)	0.01274(7)	0.01190(11)	0.01533(11)	0.01099(11)	-0.00080(8)	0.00021(8)	-0.00030(8)
323	P	0.39727(4)	0.40719(2)	0.22699(9)	0.01341(11)	0.0161(2)	0.0118(2)	0.0123(2)	0.00082(17)	-0.00014(17)	0.00119(17)
324	OW1	0.10778(19)	3/4	0.2453(4)	0.0234(4)	0.0234(10)	0.0272(11)	0.0198(10)	0.000	-0.0023(9)	0.000
325	H1	0.110(2)	0.7142(14)	0.159(5)	0.050						
326	OW2	0.1076(2)	1/4	0.3479(5)	0.0322(5)	0.0193(10)	0.0509(15)	0.0264(12)	0.000	0.0016(10)	0.000
327	H2a	0.037(3)	1/4	0.301(8)	0.050						
328	H2b*	0.116(4)	0.221(2)	0.471(9)	0.050						
329	OW3	0.34053(15)	0.66755(9)	0.3260(3)	0.0304(4)	0.0298(9)	0.0265(8)	0.0347(9)	0.0030(7)	0.0027(7)	0.0080(6)
330	H3a	0.392(2)	0.6355(15)	0.390(6)	0.050						
331	H3b*	0.282(5)	0.636(3)	0.280(11)	0.050						
332	H3c*	0.377(9)	0.706(4)	0.38(2)	0.050						
333	H3d*	0.349(10)	0.670(7)	0.158(10)	0.050						
334	O4	0.35988(13)	0.32957(7)	0.2834(3)	0.0228(3)	0.0322(8)	0.0169(7)	0.0193(7)	0.0023(5)	-0.0081(6)	-0.0059(6)
335	O5	0.10004(15)	0.57806(7)	0.4318(3)	0.0302(3)	0.0555(9)	0.0201(7)	0.0149(7)	-0.0037(5)	-0.0065(7)	0.0120(6)
336	O6	0.02485(12)	0.42282(7)	0.1428(3)	0.0220(3)	0.0147(6)	0.0181(6)	0.0334(8)	-0.0052(6)	0.0028(6)	-0.0020(5)
337	O7	0.30179(11)	0.46036(7)	0.3610(2)	0.0181(3)	0.0151(6)	0.0234(7)	0.0158(6)	-0.0036(5)	-0.0028(5)	0.0048(5)
338	* Assigned site occupancies: Mn: $\text{Mn}_{0.819}\text{Fe}_{0.080}\text{Mg}_{0.063}\text{Al}_{0.008}\text{Ca}_{0.004}$ ; Zn: $\text{Zn}_{0.898}\text{Mn}_{0.077}\text{Fe}_{0.017}$ ; H2b: 0.5; H3b: 0.5; H3c: 0.25; H3d: 0.25. All										
339	other sites assigned full occupancy,										

340



341 Table 5. Selected bond distances (Å) in nizamoffite.  
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344	Mn–O4(×2)	2.1191(13)	Zn–O5	1.9016(13)	P–O4	1.5155(14)
345	Mn–OW2	2.1543(23)	Zn–O6	1.9196(13)	P–O5	1.5179(15)
346	Mn–OW1	2.1552(20)	Zn–O7	1.9896(12)	P–O6	1.5376(13)
347	Mn–OW3(×2)	2.2263(16)	Zn–O7	2.0004(13)	P–O7	1.5681(13)
348	<Mn–O>	2.1762	<Zn–O>	1.9528	<P–O>	1.5348

349

350 Hydrogen bonds (D = donor, A = acceptor)

351	D–H	d(D–H)	d(H···A)	<DHA	d(D···A)	A	<HDH	H–D–H
352	OW1–H1 (×2)	0.79(2)	2.09(3)	146(3)	2.782(2)	O4	113	H1–OW1–H1
353	OW2–H2a	0.79(3)	2.43(3)	142.5(6)	3.093(2)	O4		
354	OW2–H2b (×2)	0.83(4)	2.10(4)	166(5)	2.911(3)	OW3	109	H2a–OW2–H2b
355	OW3–H3a	0.87(3)	1.89(3)	159(3)	2.723(2)	O6		
356	OW3–H3b	0.89(4)	2.34(5)	143(5)	3.096(2)	O5	95	H3a–OW3–H3b
357	OW3–H3c	0.85(5)	2.38(8)	136(9)	3.047(3)	OW3	100	H3a–OW3–H3c
358	OW3–H3d	0.85(5)	2.21(9)	140(11)	2.911(3)	OW2	110	H3a–OW3–H3d

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363 Table 6. Bond-valence analysis for nizamoffite. Values are expressed in valence units.

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	OW1	OW2	OW3	O4	O5	O6	O7	$\Sigma$
Mn	0.32	0.32	0.26 $\times$ 2 $\rightarrow$	0.35 $\times$ 2 $\rightarrow$				1.86
Zn					0.58	0.55	0.45, 0.44	2.02
P				1.32	1.31	1.24	1.14	5.01
H1	0.82 $\times$ 2 $\downarrow$			0.18				1.00
H2a		0.91		0.09				1.00
H2b		0.86	0.14					1.00
H3a			0.80			0.20		1.00
H3b			0.45		0.05			0.50
H3c			0.23, 0.02					0.25
H3d		0.03	0.22					0.25
$\Sigma$	1.96	2.12	2.12	1.94	1.94	1.99	2.03	

*Note:* Bond strengths are taken from Brown and Altermatt (1985) and are adjusted for site occupancies; hydrogen bond strengths are based on O $\cdots$ O bond lengths and are also from Brown and Altermatt (1985).

365

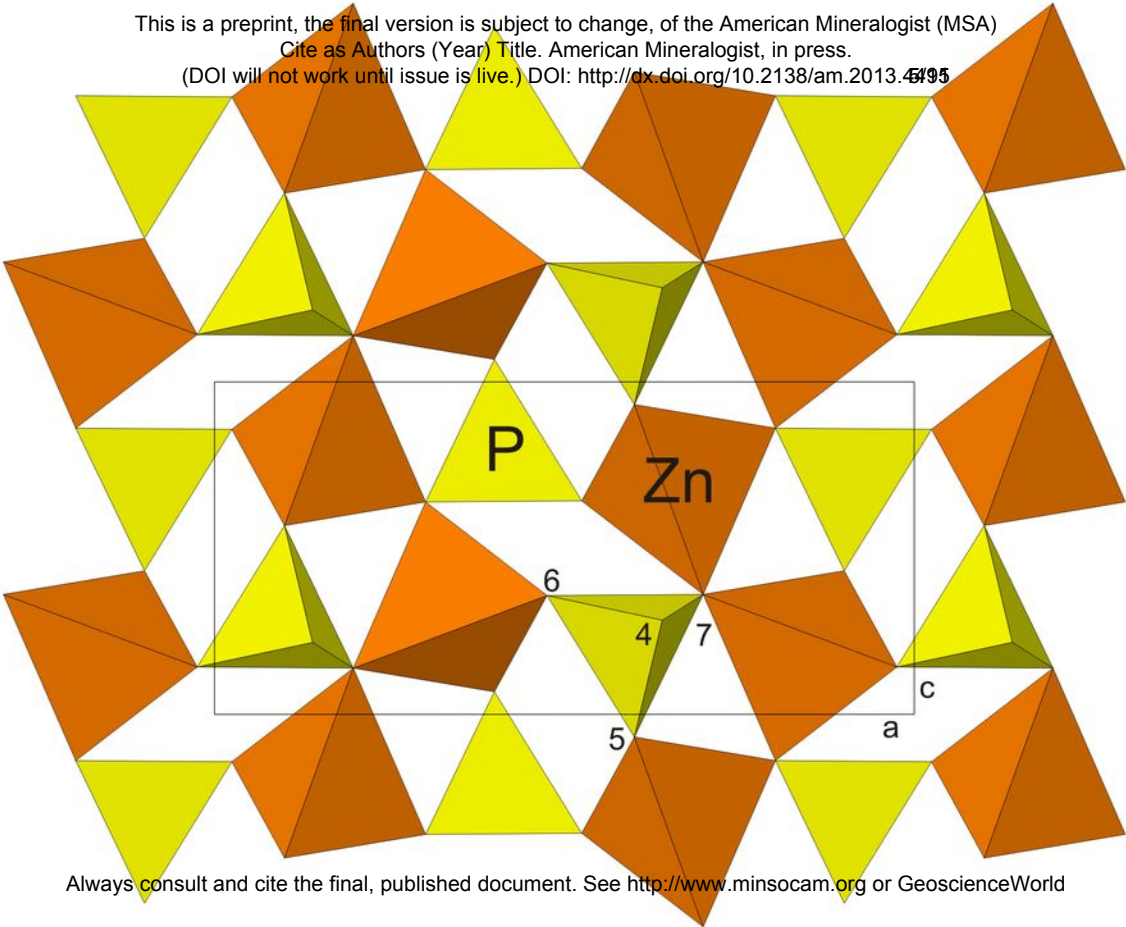


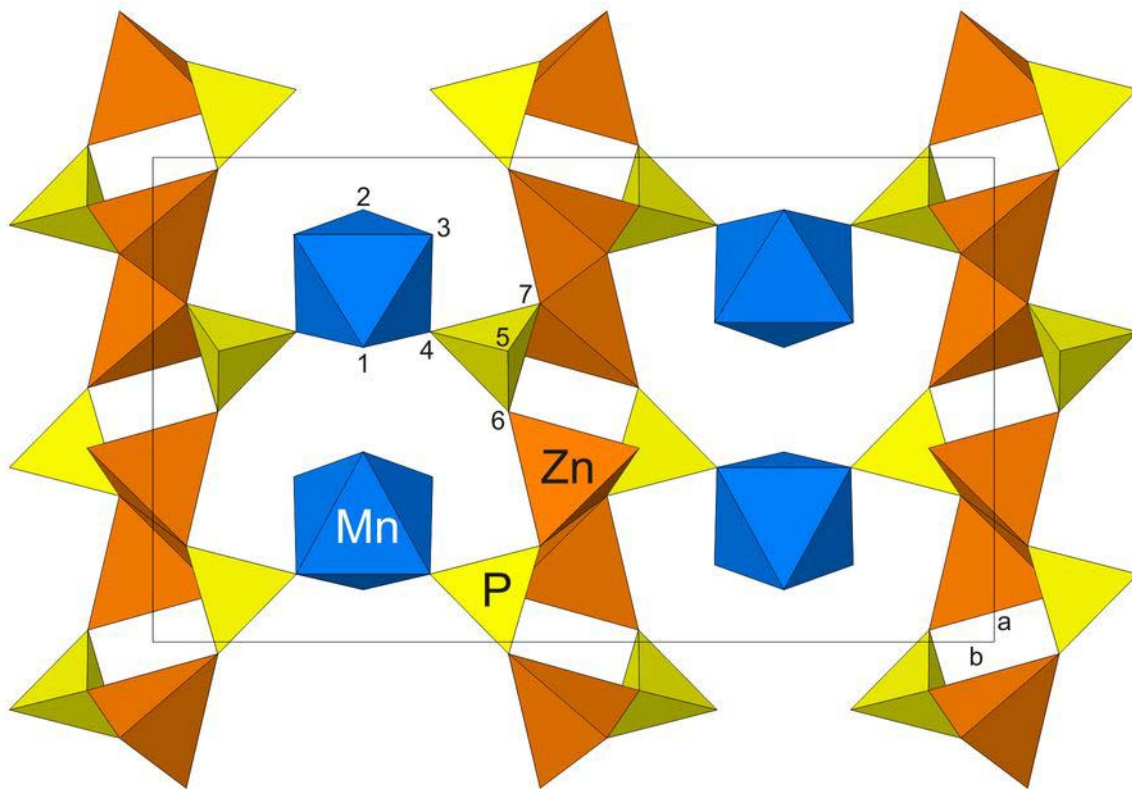
$2\bar{3}0$   $100$   $230$   $010$

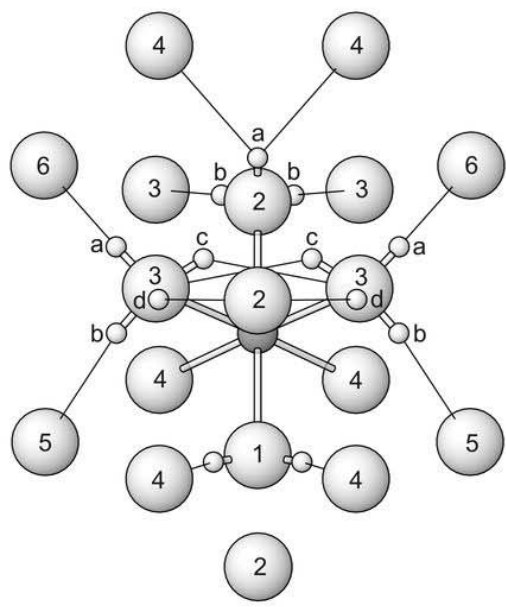
$111$

$11\bar{1}$

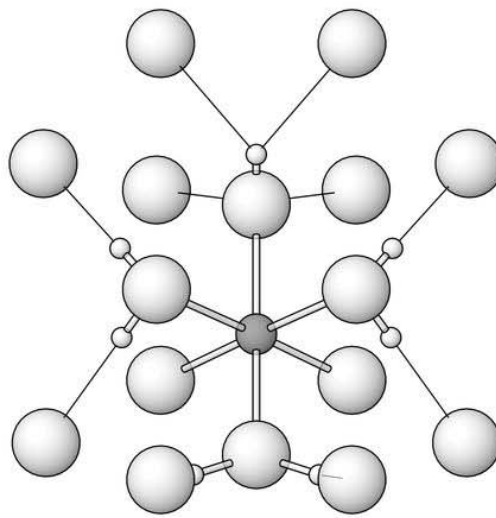
$03\bar{1}$



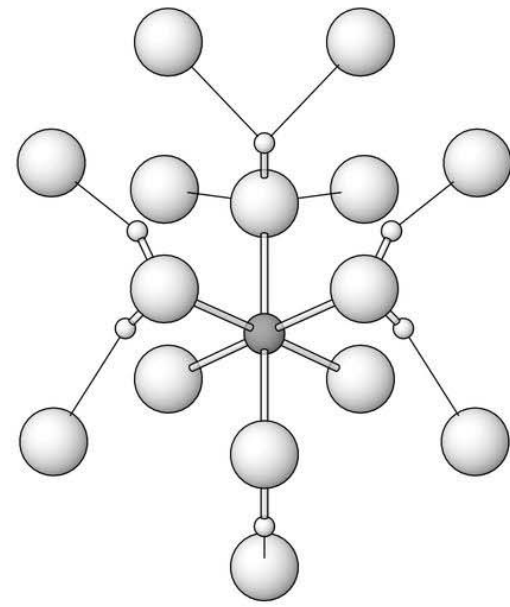




nizamoffite



$\alpha$ -hopeite



$\beta$ -hopeite