Jahnsite-(NaFeMg), a new mineral from the Tip Top mine, Custer County, South Dakota: Description and crystal structure

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ABSTRACT

Jahnsite-(NaFeMg), $NaFe^{3+}Mg_2Fe_2^{3+}(PO_4)_4(OH)_2 \cdot 8H_2O$, space group $P2/a$, $a = 15.0811(16)$, $b = 7.1403(8)$, $c = 9.8299(11)$ Å, $\beta = 110.445(1)°$, $V = 991.8(2)$ Å^3, and $Z = 2$, is a new mineral from the Tip Top mine, Custer County, South Dakota. It occurs as the dominant chemical zone in transparent pseudo-orthorhombic twinned prisms up to 1 mm long with shallow wedge-like terminations, both as isolated twinned crystals and in subparallel to divergent intergrowths. The crystals are yellow with orange-red bands just below the terminations. The mineral has a white streak, vitreous luster, Mohs hardness of 4, and good {001} cleavage. The measured density is 2.58(2) g/cm^3, and the calculated density is 2.608 g/cm^3. It is optically biaxial (–), with $\alpha = 1.632(1)$, $\beta = 1.669(1)$, $\gamma = 1.671(1)$ (589 nm); $2V$ (meas.) = 25(5)°, $2V$ (calc.) = 26°; dispersion: $r > v$, very strong; orientation: $Y = b$, $Z \wedge a = +28°$ (in β obtuse); pleochroism: X = colorless, Y and Z = beige; $Y = Z > X$. Electron microprobe analyses provided: Na_2O 2.82, CaO 0.34, MnO 0.32, MgO 10.27, Fe_2O_3 27.35, P_2O_5 35.93, H_2O 21.58 (calc.), total 98.61, which in terms of the general formula for the whiteite-jahnsite group $XM1M2_2M3_2(PO_4)_4(OH)_2 \cdot 8H_2O$, yields the empirical formula: $(Na_{0.72}Ca_{0.05}Mn_{0.04}^{2+})(Fe_{0.72}^{3+}Mg_{0.01})Mg_{2.00}Fe_{2.00}^{3+}(PO_{3.77}OH_{0.23})_4(OH)_2 \cdot 8H_2O$. Crystal structure refinement ($R_1 = 0.041$) supports these cation site assignments. Typical crystals have as many as five chemical zones from base to termination corresponding to the following jahnsite species: jahnsite-(NaMnMg), jahnsite-(NaFeMg), jahnsite-(CaMnMg), jahnsite-(NaFeMg), jahnsite-(CaMgMg). The characterization of the new mineral jahnsite-(NaFeMg) is based upon the second zone listed, which corresponds to roughly 80% of the crystal volume. Jahnsite-(NaMnMg) and jahnsite-(CaMgMg) also represent new species; however, the very small volume of these zones is insufficient to permit complete characterization of these species. Jahnsite-(NaFeMg) is the first member of the whiteite-jahnsite group in which a monovalent cation (Na$^+$) predominantly occupies the X site and a trivalent cation (Fe^{3+}) the M1 site. The structure differs from that determined for jahnsite-(CaMnMg) in that the X site is [8]-coordinated and the M1 and P1 polyhedra exhibit greater distortions caused by cation-cation repulsion across their shared edges. The determination of H positions allows the elucidation of a definitive H-bonding scheme.

Keywords: Jahnsite, Tip Top mine, new mineral, crystal structure, whiteite-jahnsite group, crystal chemistry, pegmatite phosphate

INTRODUCTION

Jahnsite was first described as a new mineral from the Tip Top pegmatite by Moore (1974), and the atomic structure of the mineral was determined by Moore and Araki (1974). The original jahnsite was renamed jahnsite-(CaMnMg) by Moore and Ito (1978) as part of the delineation of a naming scheme for members of the whiteite-jahnsite group. This scheme is based upon the dominant cations in the four non-tetrahedral cation sites in the structure, designated X, M1, M2, and M3. (Actually, M2 and M3 each consist of two very similar cation sites.) The generalized formula is $XM1M2_2M3_2(PO_4)_4(OH)_2 \cdot 8H_2O$. The M3 site determines the root name, whiteite if M3 is Al^{3+} and jahnsite if M3 is Fe^{3+}. The chemical elements in the remaining three sites, X, M1, and M2 are combined into the extension.

Table 1 lists all of the reported members of the whiteite-jahnsite group, including three that are not named in accordance with the scheme presented by Moore and Ito (1978) and adopted by the IMA. Also included in this table are three new members reported in this study, although only one, jahnsite-(NaFeMg), has been found in sufficient quantity to be completely characterized and officially named as a new species.

The new mineral and name have been approved by the Commission on New Minerals, Nomenclature, and Classification of the International Mineralogical Association (IMA 2007-016). The three co-type specimens are housed in the mineral collection of the Natural History Museum of Los Angeles County (catalog numbers 58590, 58591, and 58592).

OCCURRENCE

All known specimens of the new jahnsite species came from a single football-sized rock, consisting mainly of heterosite

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TABLE 1. Members of the whiteite-jahnsite group

Species Name	Structure site assignments				Reference
	X	M1	M2	M3	
Whiteite-(CaFeMg)	Ca^{2+}	Fe^{2+}	Mg^{2+}	Al^{3+}	Moore and Ito (1978)
Whiteite-(CaMnMg)	Ca^{2+}	Mn^{2+}	Mg^{2+}	Al^{3+}	Grice et al. (1989)
Whiteite-(MnFeMg)	Mn^{2+}	Fe^{2+}	Mg^{2+}	Al^{3+}	Moore and Ito (1978)
Rittmannite	Mn^{2+}	Mn^{2+}	Fe^{2+}	Al^{3+}	Marzoni Fecia Di Cossato et al. (1989)
Jahnsite-(CaMnMg)	Ca^{2+}	Mn^{2+}	Mg^{2+}	Fe^{3+}	Moore (1974), Moore and Ito (1978)
Jahnsite-(CaMnFe)	Ca^{2+}	Mn^{2+}	Fe^{2+}	Fe^{3+}	Moore and Ito (1978)
Jahnsite-(CaMnMn)	Ca^{2+}	Mn^{2+}	Mn^{2+}	Fe^{3+}	Grice et al. (1990)
Jahnsite-(MnMnMn)	Mn^{2+}	Mn^{2+}	Mn^{2+}	Fe^{3+}	Moore and Ito (1978)
"Jahnsite-(CaFeFe)"*	Ca^{2+}	Fe^{2+}	Fe^{2+}	Fe^{3+}	Matsubara (2000)
"Jahnsite-(CaMgMg)"†	Ca^{2+}	Mg^{2+}	Mg^{2+}	Fe^{3+}	This study
"Jahnsite-(NaMnMg)"†	Na^{+}	Mn^{3+}	Mg^{2+}	Fe^{3+}	This study
Jahnsite-(NaFeMg)	Na^{+}	Fe^{3+}	Mg^{2+}	Fe^{3+}	This study
"Kaluginite"*	Mn^{2+}	Mn^{2+}	Mg^{2+}	Fe^{3+}	Chesnokov et al. (1989)
Keckite‡	Ca^{2+}	Mn^{2+}	$Fe^{2+}Mn^{2+}$	Fe^{3+}	Mücke (1979)

* Species published, but never approved by the IMA.
† Reported in this study based upon chemical analyses of narrow zones; not voted upon by the IMA Commission on New Minerals, Nomenclature and Classification.
‡ The ideal formula originally proposed for keckite, $CaMn_2^{2+}Fe_3^{3+}(PO_4)_4(OH)_3 \cdot 3H_2O$, differs from the general formula for the jahnsite group. A formula for keckite compatible with the general group formula can be derived by discarding the original dubious assumption that all Fe is ferric and by hypothesizing greater water content (H_2O was originally calculated by difference). The formula for keckite (with equal amounts of Mn and Fe in the M2 sites) thereby derived is $CaMn^{2+}(Mn^{2+}Fe^{2+})_2Fe_2^{3+}(PO_4)_4(OH)_2 \cdot 8H_2O$. Unless Mn^{2+} and Fe^{2+} can be proven to be ordered in the two very similar M2 sites, keckite should probably be considered an intermediate between jahnsite-(CaMnMn) and jahnsite-(CaMnFe) and, therefore, discredited.

FIGURE 1. Crystal drawing of jahnsite-(NaFeMg) in non-standard clinographic orientation. Twinning by reflection on {001} is evidenced by the reentrant angle at the base of the crystal drawing, although reentrant angles are generally only manifest as striations on the terminal {100} faces, probably resulting from polysynthetic twinning.

and presumed to be a fragment of highly altered and oxidized triphylite. This rock was collected from the dump of the Tip Top mine, Custer County, South Dakota, in July 2005 by one of the authors (T.A.L.) and Buford Nichols of Houston, Texas. Vugs in the heterosite contain the jahnsite in association with several other secondary phosphate minerals including leucophosphite, dufrénite, barbosalite, rockbridgeite, mitridatite, and ushkovite. All of these species were presumably formed as late-stage hydrothermal decomposition products of triphylite. The jahnsite crystals appear to be the latest of the species to form.

The Tip Top mine is located just southwest of the center of Sec. 8, T3S, R4E, about 8.5 km southwest of Custer, Custer County, South Dakota (43°42'56"N, 103°40'10"W). The mine, which exploits a complex granitic pegmatite, has produced commercial quantities of muscovite, microcline perthite, beryl, montebrasite-amblygonite, spodumene, and columbite-tantalite, but is best known by mineralogists for its complex assemblages of unusual secondary phosphate minerals. Papers by Campbell and Roberts (1986) and Loomis and Campbell (2002) describe the pegmatite and its mineralogy, with particular emphasis on the secondary phosphates.

PHYSICAL AND OPTICAL PROPERTIES

The crystals of jahnsite are prismatic along [100] and exhibit ubiquitous twinning, both simple contact and polysynthetic by reflection on {001}. The twinning combines with the prism forms {011} and {001} and the terminal form {100} to yield six-sided pseudo-orthorhombic prisms with shallow wedge-like terminations (Fig. 1). Striations parallel to [010], often observed on the {100} faces, are probably small reentrants resulting from polysynthetic twinning. Crystals occur as isolated twinned individuals and in subparallel to divergent intergrowths. They are typically up to 0.5
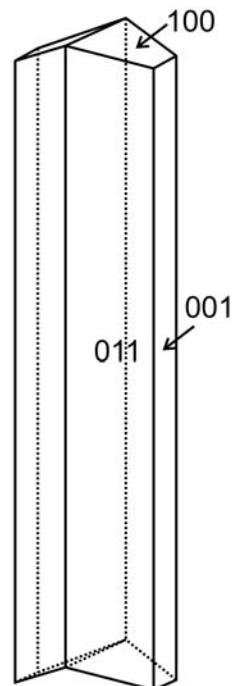
$\times 0.1 \times 0.1$ mm, but some crystals reach 1 mm in length.

The crystals are yellow with orange-red bands near their terminations. The streak is white. The luster is vitreous and most crystals exhibit good transparency. The crystals are brittle with splintery fracture and a Mohs hardness of about 4. There is one good cleavage, {001}. The density measured by sink-float in sodium polytungstate solution is 2.58(2) g/cm³ and that calculated from the empirical formula is 2.608 g/cm³. Crystals slowly dissolve in cold dilute HCl.

The mineral is optically biaxial (–) with optical constants measured in sodium light (589 nm): $n_\alpha = 1.632(1)$, $n_\beta = 1.669(1)$, $n_\gamma = 1.671(1)$. The measured $2V$ is 25(5)°, which compares well to the calculated value, 26°. Very strong $r > v$ dispersion was observed. The optical orientation is $Y = b$, $Z \wedge a = +28°$ (in β obtuse). The crystals are slightly, but noticeably, pleochroic: X = colorless, Y and Z = beige; $Y = Z > X$.

The color banding observed is a visual clue to chemical zonation, as borne out by the chemical analyses and backscatter electron images reported in the next section. The central portion of crystals, between their bases and terminations and amounting to roughly 80% of their volumes, corresponds to the new species jahnsite-(NaFeMg). For density and optical studies, the bases and terminations of crystals were removed, so that these data are for only jahnsite-(NaFeMg).

CHEMISTRY

Quantitative chemical analyses were performed by electron microprobe (WDS mode, 15 kV, 20 nA, 5 µm beam diameter).

Backscatter electron images showed all crystals studied to be zoned, with typical crystals exhibiting five distinct zones from base (zone 1) to termination (zone 5). The complete probe analyses for zone 2, the principal zone corresponding to the new mineral jahnsite-(NaFeMg) are given in Table 2. The site assignments shown in Table 2 are made using the approach recommended by Moore and Ito (1978), which calls for the smallest trivalent cations to be placed in M3 until that site is filled, then site M2, etc. until the largest remaining cations are placed in X. This is in accord with the structure analysis, except that refined site occupancies suggest that the M1, M2, and M3 sites are all slightly less than fully occupied.

The empirical formula (based on P = 4 apfu and sufficient H for charge balance) is $(Na_{0.72}Ca_{0.05}Mn^{2+}_{0.04})(Fe^{3+}_{0.72}Mg_{0.01})Mg_{2.00}Fe^{3+}_{2.00}$ $(PO_{3.77}OH_{0.23})_4(OH)_2 \cdot 8H_2O$. Note that assigning the PO_4 group some PO_3OH character is supported by the results of the structure determination, which indicate most of the O atoms associated with the phosphate groups to be slightly undersaturated with respect to valence balance. The end-member formula is $NaFe^{3+}Mg_2Fe^{3+}_2(PO_4)_4(OH)_2 \cdot 8H_2O$, which requires: Na_2O 3.89, MgO 10.11, Fe_2O_3 30.05, P_2O_5 35.61, H_2O 20.34, Total 100.00 wt%.

The cation site assignments of all five zones, based upon EMP analyses and using the assignment approach recommended by Moore and Ito (1978), are given in Table 3. The crystals exhibited rapid sodium migration due to the effects of the electron beam. Zones 2 and 5 were large enough so that the crystal could be moved under the beam during the analyses to minimize Na modification. BSE element maps showed zone 3 to have a very low Na content and zones 1 and 4 to have significant Na contents, but somewhat lower than zone 2. The Na contents indicated in the cation site assignments (Table 3) for zones 2, 3, and 5 are considered reasonably accurate based upon the EMP analyses, while those for zones 1 and 4 have been adjusted up to compensate for Na modification.

The crystal-structure data were obtained from a crystal fragment from which the base and termination had been removed, and the results of the structure determination are consistent with zone 2 chemistry, jahnsite-(NaFeMg).

X-RAY CRYSTALLOGRAPHY AND STRUCTURE REFINEMENT

X-ray powder-diffraction data (Table 4) were obtained using a Gandolfi camera (114.6 mm diameter, Ni-filtered Cu$K\alpha$ radiation). The data show good agreement with the pattern calculated from the structure.

Structure data collection was performed on a Bruker PLATFORM 3-circle goniometer equipped with a 1K SMART CCD detector. After many unsuccessful attempts to separate an untwinned crystal fragment for structure data collection, it was decided to use a simple contact twinned crystal with one dominant individual. A full sphere of three-dimensional data were collected for the larger of the twin individuals. The only overlap in the twinned lattices occurs in the 0kl plane, so these reflections were thrown out. Fifty duplicate frames, acquired at the end of the data collection, indicated that no significant decay had taken place. The measured intensities were corrected for Lorentz and polarization effects using the program SAINT and an empirical absorption correction was applied using the program SADABS (Bruker 1997). The SHELXL97 software (Sheldrick 1997) was used for the refinement of the structure.

Metal atoms were assigned to the cation sites based upon bond distance and valence balance considerations. While a small amount of cation mixing is possible (see discussion below), no attempt was made to adjust for this in the structure refinements other than to refine cation site occupancies. With all non-hydrogen atoms located and refined anisotropically at full occupancies, the R_1 (conventional R factor) converged to 4.55% for 2226 reflections with $F_o > 4\sigma(F_o)$. Because the chemical analyses suggested less than full occupancies in some of the cation sites, the occupancies of these sites were refined yielding slightly less than full occupancies for all except the X site, with R_1 improving to 4.41%. (Small amounts of Ca and Mn in the X site may account for this site refining to full occupancy.) The difference map showed peaks assignable to all likely H atom positions. These positions were refined with O(donor)-H distances restrained to 0.9 Å and the H-H distance corresponding to water molecules restrained to 1.45 Å, in each case with standard deviations of 0.03. In the final refinement, R_1 converged to 4.14%. Table 5 gives the details of the data collection and structure refinement; Table 6, the final fractional coordinates and isotropic displacement parameters; Table 7, the anisotropic displacement parameters; Table 8, interatomic distances and angles; Table 9, hydrogen bond distances and angles; and Table 10, bond valences.

DISCUSSION OF THE STRUCTURE

The atomic structure determination by Moore and Araki (1974) for jahnsite-(CaMnMg) was heretofore the only the atomic structure determination for a whiteite-jahnsite group species. The structure determination in this study for jahnsite-(NaFeMg) confirms the general structural motif reported by Moore and Araki. The structure is based on a chain of $M3^{3+}$ octahedra along **b** linked by sharing trans-OH corners and by sharing corners of

TABLE 2. Electron microprobe analyses for zone 2, jahnsite-(NaFeMg)

	Analyses (wt%)				Atoms	Structure site assignments			
	1	2	3	Avg.	(P = 4)	X Na	M1 Fe1	M2 Mg1 and Mg2	M3 Fe2 and Fe3
Na_2O	3.17	2.34	2.94	2.82	0.719	0.719			
CaO	0.34	0.31	0.38	0.34	0.048	0.048			
MnO	0.20	0.44	0.33	0.32	0.036	0.036			
MgO	10.10	10.40	10.30	10.27	2.013		0.013	2.000	
Fe_2O_3*	27.43	27.87	26.76	27.35	2.720		0.720		2.000
P_2O_5	35.50	35.70	36.60	35.93	4.000				
H_2O†	21.14	21.22	22.40	21.58	18.927				
Total	97.88	98.28	99.71	98.61		0.803	0.733	2.000	2.000

Notes: Standards = Amelia albite for Na, synthetic $Ca_2P_2O_7$ for Ca and P, Mn-metal for Mn, natural olivine for Mg and Fe.
* All Fe is calculated as Fe^{3+} as this is consistent with the results of the structure analysis, as well as with the oxidized nature of the mineral assemblage.
† H_2O calculated from the crystal structure analysis and charge balance.

TABLE 3. Cation site contents for zones observed in jahnsite crystals from base (zone 1) to termination (zone 5)

Zone	Vol%	Contents of X*, M1, M2, and M3 sites	Jahnsite-
1	3	$(Na_{0.50}Ca_{0.19}Mn^{2+}_{0.12})(Mn^{2+}_{1.00})(Mg_{1.56}Mn^{2+}_{0.34}Fe^{3+}_{0.10})(Fe^{3+}_{2.00})$	(NaMnMg)
2	80	$(Na_{0.72}Ca_{0.05}Mn^{2+}_{0.04})(Fe^{3+}_{0.72}Mg_{0.01})(Mg_{2.00})(Fe^{3+}_{2.00})$	(NaFeMg)
3	8	$(Ca_{0.48}Mn^{2+}_{0.25}Na_{0.01})(Mn^{2+}_{1.00})(Mg_{1.74}Mn^{2+}_{0.26})(Fe^{3+}_{1.82}Mg_{0.18})$	(CaMnMg)
4	3	$(Na_{0.50}Ca_{0.26})(Fe^{3+}_{0.64}Mg_{0.26}Mn^{2+}_{0.02})(Fe^{3+}_{2.00})$	(NaFeMg)
5	6	$(Ca_{0.56}Na_{0.44})(Mg_{0.39}Fe^{3+}_{0.34}Ca_{0.09}Mn^{2+}_{0.01})(Mg_{2.00})(Fe^{3+}_{2.00})$	(CaMgMg)

* Sodium contents for zones 1 and 4 have been adjusted up to compensate for rapid Na migration in the electron beam (see text).

TABLE 4. Observed and calculated X-ray powder-diffraction pattern for jahnsite-(NaFeMg)

I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl
100	9.218	9.211	100	0 0 1
5	7.138	7.140	7	0 1 0
5	6.370	6.373	5	1 $\bar{1}$ 0
10	5.678	5.676	9	1 1 1
15	5.022	5.022	18	2 1 0
25	4.884	4.893	25	1 1 1
10	4.607	4.605	13	0 0 2
5	4.046	4.048	5	1 1 2
15	3.931	3.932	12	$\underline{3}$ 1 0
25	3.537	3.544	11	$\bar{3}$ 1 2
		3.533	14	$\bar{4}$ 0 0
10	3.450	3.444	13	$\bar{4}$ 0 2
10	3.293	3.287	11	$\underline{3}$ 1 1
10	3.172	3.170	6	2 2 1
		3.166	3	4 1 0
25	2.973	2.970	25	$\bar{4}$ 0 1
20	2.854	2.865	14	$\bar{4}$ 0 3
		2.858	8	3 1 3
70	2.819	2.822	67	$\underline{0}$ 2 2
25	2.593	2.592	25	4 2 1
10	2.338	2.340	5	$\underline{6}$ 1 2
		2.339	4	4 0 4
10	2.001	2.005	8	$\underline{4}$ 2 2
5	1.956	1.956	6	4 2 4
20	1.933	1.935	13	$\underline{0}$ 2 4
		1.934	4	$\underline{4}$ 0 5
20	1.885	1.884	14	8 0 2
10	1.785	1.785	8	0 4 0
15	1.584	1.583	10	$\underline{8}$ 2 0
5	1.550	1.551	5	8 2 4
5	1.534	1.535	4	0 0 6
		1.530	4	4 4 1
5	1.519	1.520	6	$\underline{4}$ 2 4
5	1.484	1.484	6	4 2 6

TABLE 5. Data collection and structure refinement details for jahnsite-(NaFeMg)

Diffractometer	Bruker SMART Platform CCD
X-ray radiation/power	Mo$K\alpha$ ($\lambda = 0.71073$ Å)/50 kV, 45 mA
Temperature	298(2) K
Space group	$P2/a$
Unit-cell dimensions	$a = 15.0811(16)$ Å
	$b = 7.1403(8)$ Å
	$c = 9.8299(11)$ Å
	$\beta = 110.445(1)°$
Volume	991.8(2) Å³
Z	2
Absorption coefficient	2.693 mm⁻¹
$F(000)$	787
Crystal size ($\mathbf{a} \times \mathbf{b} \times \mathbf{c}$)	$0.140 \times 0.045 \times 0.045$ mm
Frame number/width/time	1080/0.3° in ω/30 s
θ range	4.06 to 30.70°
Index ranges	$-21 \le h \le 21, -10 \le k \le 10, -13 \le l \le 14$
Reflections collected	9126
Independent reflections	2789
Reflections, $F_o > 4\sigma(F_o)$	2226
Completeness to $\theta = 28.26°$	90.3%
Refinement method	Full-matrix least-squares on F^2
Parameters refined	201
GooF†	1.082
R indices [$F_o > 4\sigma(F_o)$]	$R_1 = 4.14\%$, $wR_2 = 11.97\%$
R indices (all data)	$R_1 = 5.55\%$, $wR_2 = 12.65\%$
Largest diff. peak/hole	$+0.58/-0.54$ e/Å³

Notes: $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$. GooF $= S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where a is 0, b is 12.994 and P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

TABLE 6. Atomic coordinates, occupancies and equivalent isotropic displacement parameters (Å²) for jahnsite-(NaFeMg)

	x	y	z	U_{eq}	Occupancy
Na (X)	1/4	0.9701(4)	0	0.0203(5)	
Fe1(M1)	1/4	0.4713(1)	0	0.0083(3)	0.920(5)
Mg1 (M2)	1/2	0	1/2	0.0125(7)	0.970(11)
Mg2 (M2)	1/4	0.5057(3)	1/2	0.0111(7)	0.964(11)
Fe2 (M3)	0	0	0	0.0084(3)	0.962(5)
Fe3 (M3)	0	1/2	0	0.0085(3)	0.966(5)
P1	0.1870(1)	0.2677(1)	0.1856(1)	0.0089(2)	
P2	0.0800(1)	0.7419(1)	0.7963(1)	0.0093(2)	
O1	0.2789(2)	0.2510(4)	0.1489(3)	0.0157(6)	
O2	0.2082(2)	0.3103(5)	0.3435(3)	0.0187(6)	
O3	0.1264(2)	0.0929(4)	0.1411(3)	0.0176(6)	
O4	0.1405(2)	0.4378(4)	0.0810(3)	0.0120(6)	
O5	0.1837(2)	0.6682(4)	0.8599(3)	0.0165(6)	
O6	0.0574(2)	0.7822(4)	0.6364(3)	0.0149(6)	
O7	0.0750(2)	0.9217(4)	0.8777(3)	0.0166(6)	
O8	0.0126(2)	0.5928(4)	0.8173(3)	0.0133(6)	
OH	0.0274(2)	0.7509(4)	0.0992(3)	0.0140(6)	
OW1	0.2272(3)	0.7264(5)	0.3420(4)	0.0270(8)	
OW2	0.4484(3)	0.2126(5)	0.3482(4)	0.0298(8)	
OW3	0.6269(3)	0.9869(5)	0.4565(5)	0.0285(8)	
OW4	0.3907(2)	0.5152(5)	0.5161(4)	0.0211(7)	
HOH	0.996(5)	0.749(10)	0.162(6)	0.050	
HW1a	0.258(4)	0.717(10)	0.278(6)	0.05	
0HW1b	0.167(2)	0.748(10)	0.293(6)	0.050	
HW2a	0.434(4)	0.298(8)	0.405(6)	0.050	
HW2b	0.395(3)	0.201(9)	0.269(5)	0.05	
0HW3a	0.618(5)	0.046(9)	0.371(5)	0.05	
0HW3b	0.659(4)	0.884(6)	0.452(7)	0.050	
HW4a	0.416(4)	0.605(8)	0.478(6)	0.050	
HW4b	0.425(4)	0.491(9)	0.606(4)	0.050	

TABLE 7. Anisotropic displacement parameters (Å²) for jahnsite-(NaFeMg)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	0.0204(12)	0.0136(12)	0.0204(13)	0	−0.0012(10)	0
Fe1	0.0067(4)	0.0096(4)	0.0088(4)	0	0.0031(3)	0
Mg1	0.0131(11)	0.0116(11)	0.0116(11)	−0.0024(7)	0.0027(8)	−0.0004(7)
Mg2	0.0124(11)	0.0120(11)	0.0088(11)	0	0.0034(8)	0
Fe2	0.0095(4)	0.0062(4)	0.0098(4)	−0.0006(3)	0.0037(3)	−0.0000(3)
Fe3	0.0080(4)	0.0072(4)	0.0104(4)	0.0007(3)	0.0036(3)	0.0001(3)
P1	0.0082(4)	0.0094(4)	0.0085(4)	−0.0009(3)	0.0023(3)	−0.0003(3)
P2	0.0089(4)	0.0100(5)	0.0091(4)	0.0007(3)	0.0034(3)	0.0012(3)
O1	0.009(1)	0.021(2)	0.018(2)	0.004(1)	0.005(1)	0.005(1)
O2	0.023(2)	0.020(2)	0.014(2)	−0.001(1)	0.007(1)	0.001(1)
O3	0.016(1)	0.013(1)	0.019(2)	−0.001(1)	0.000(1)	−0.005(1)
O4	0.009(1)	0.014(1)	0.013(1)	0.003(1)	0.004(1)	0.001(1)
O5	0.010(1)	0.022(2)	0.017(2)	0.004(1)	0.004(1)	0.004(1)
O6	0.020(2)	0.013(1)	0.011(1)	0.003(1)	0.005(1)	0.001(1)
O7	0.021(2)	0.014(1)	0.019(2)	−0.003(1)	0.012(1)	−0.002(1)
O8	0.013(1)	0.012(1)	0.015(1)	0.002(1)	0.006(1)	−0.001(1)
OH	0.017(1)	0.010(1)	0.017(1)	−0.002(1)	0.008(1)	0.001(1)
OW1	0.033(2)	0.027(2)	0.025(2)	0.006(1)	0.015(2)	0.010(2)
OW2	0.034(2)	0.022(2)	0.020(2)	0.003(1)	−0.006(1)	−0.003(1)
OW3	0.024(2)	0.026(2)	0.039(2)	−0.005(2)	0.016(2)	−0.001(1)
OW4	0.017(2)	0.022(2)	0.024(2)	0.006(1)	0.007(1)	−0.002(1)

to M2-(O,H₂O)₆ octahedra (see Figs. 2 and 3).

The assignments of Na to the X site, Fe^{3+} to the M1 site, Mg^{2+} to the M2 sites (Mg1 and Mg2), and Fe^{3+} to the M3 sites (Fe2 and Fe3) is borne out by the bond lengths (Table 8) and valence balance sums (Table 10), although the similarities in sizes of the M1 and M2 sites leaves open the possibility that there is some mixing of cations between these sites. The valence sums for the M2 sites (2.148 and 2.144) are a bit high suggesting that a small amount of Fe^{3+} may occupy these sites, and the valence sum for the M1 sites (2.762) is low suggesting some Mg^{2+} at this site and/or significantly lower than full occupancy.

PO₄ tetrahedra arranged along the chains. The structure possesses dense slabs of $[XM1M3_2(OH)_2(PO_4)_4]^{4-}$ oriented parallel to {001}, which are bridged in the **c** direction by PO₄ corner-sharing

TABLE 8. Selected bond distances (Å) for jahnsite-(NaFeMg)

Na-O1 (×2)	2.430(4)	Fe1-O5 (×2)	1.978(3)	P1-O2	1.502(3)
Na-O7 (×2)	2.513(3)	Fe1-O4 (×2)	2.082(3)	P1-O3	1.518(3)
Na-O5 (×2)	2.566(4)	Fe1-O1 (×2)	2.089(3)	P1-O1	1.555(3)
Na-O3 (×2)	2.823(3)	<Fe1-O>	2.064	P1-O4	1.587(3)
<Na-O>	2.583			<P1-O>	1.541
Mg1-O6 (×2)	2.038(3)	Mg2-O2 (×2)	2.009(3)	P2-O6	1.515(3)
Mg1-OW2 (×2)	2.080(4)	Mg2-OW (×2)	2.073(3)	P2-O7	1.528(3)
Mg1-OW3 (×2)	2.104(3)	Mg2-OW1 (×2)	2.154(4)	P2-O8	1.534(3)
<Mg1-O>	2.081	<Mg2-O>	2.093	P2-O5	1.560(3)
				<P2-O>	1.535
Fe2-O7 (×2)	1.997(3)	Fe3-O8 (×2)	1.985(3)		
Fe2-OH (×2)	2.001(3)	Fe3-OH (×2)	2.012(3)		
Fe2-O3 (×2)	2.037(3)	Fe3-O4 (×2)	2.036(3)		
<Fe2-O>	2.015	<Fe3-O>	2.016		

TABLE 9. Hydrogen bond distances (Å) and angles (°) for jahnsite-(NaFeMg)

D-H	d(D-H)	d(H-A)	<D-H-A	d(D-A)	A	<H-D-H
OH-HOH	0.89(3)	2.21(4)	166(6)	3.085(5)	OW2	
OW1-HW1a	0.90(3)	1.89(4)	174(6)	2.789(5)	O5	108(4)
OW1-HW1b	0.89(3)	2.29(4)	158(6)	3.128(5)	OH	
OW2-HW2a	0.90(3)	2.13(4)	174(6)	3.026(5)	OW4	105(4)
OW2-HW2b	0.91(3)	1.77(4)	158(6)	2.635(5)	O1	
OW3-HW3a	0.90(3)	2.41(4)	122(6)	2.990(5)	OW1	105(4)
OW3-HW3b	0.89(3)	2.04(4)	153(6)	2.862(5)	O2	
OW4-HW4a	0.89(3)	1.83(4)	167(6)	2.704(5)	O6	113(4)
OW4-HW4b	0.87(3)	2.12(4)	174(6)	2.990(5)	O8	

Note: D = donor O; A = acceptor O.

FIGURE 2. Jahnsite-(NaFeMg) crystal structure viewed down [010].

FIGURE 3. [NaFe^{3+}Fe$_2^{2+}$(OH)$_2$(PO$_4$)$_4$]$^{4-}$ slabs in jahnsite-(NaFeMg) viewed perpendicular to {001}.

Coordination polyhedra for the X and M1 sites

The principle differences between the structures of jahnsite-(CaMnMg) and jahnsite-(NaFeMg) are related to the X and M1 sites. In all previously described members of the whiteite-jahnsite group (Table 1), divalent cations predominate in both the X and M1 sites, and for all of these species these sites presumably have distorted octahedral coordinations, as described for jahnsite-(CaMnMg) by Moore and Araki (1974). Jahnsite-(NaFeMg) is the first member of the group to be described in which a monovalent cation (Na$^+$) predominantly occupies the X site and a trivalent cation (Fe^{3+}) the M1 site.

In jahnsite-(NaFeMg), the X site is [8]-coordinated with six shorter bonds between 2.43 and 2.57 Å and two longer bonds of 2.82 Å. All of the O atoms coordinated to Na are within the aforementioned slab and each is bonded also to one P and one Fe. The coordination polyhedron shares edges with two P1 tetrahedra (O1-O3), two P2 tetrahedra (O5-O6), two Fe1 octahedra (O1-O1 and O5-O5) and two Fe2 octahedra (O3-O7). The polyhedron can be described as a distorted (squat) square antiprism (Fig. 4).

Moore and Araki (1974) noted that the distortions in the octahedral coordinations of the X and M1 sites are consistent with cation-cation repulsions across shared octahedral and tetrahedral edges. For the [8]-coordination about the X site in jahnsite-(NaFeMg), cation-cation repulsions are less of a factor because of the lesser charge of the X cation (Na$^+$) and the generally longer X-O distances. The shape of the coordination polyhedron appears more determined by the shape of cage created by the geometry of the linkages of the surrounding octahedra and tetrahedra of the slab. On the other hand in jahnsite-(NaFeMg), cation-cation repulsion

FIGURE 4. Sodium coordination (square antiprism) in jahnsite-(NaFeMg).

between Fe^{3+} in the M1 site and P^{5+} in the P1 site across shared octahedral-tetrahedral edges clearly plays a very important role.

The M1 octahedron shares edges with two P1 tetrahedra forming [Fe^{3+}O$_2$(PO$_4$)$_2$]$^{7-}$ units as shown in Figure 5. The cation-cation repulsion across these shared edges is manifest in much longer than average distances for the Fe1-O1, Fe1-O4, P1-O1, and P1-O4 bonds and much smaller than normal octahedral and tetrahedral angles for O1-Fe1-O4 (69.2°) and O1-P1-O4 (97.8°), respectively.

TABLE 10. Bond valence summations for jahnsite-(NaFeMg)

	O1	O2	O3	O4	O5	O6	O7	O8	OH	OW1	OW2	OW3	OW4	$\Sigma_c v$
Na	0.182		0.063		0.126		0.146							1.034*
Fe1	0.410			0.418	0.553									2.762*
Mg1						0.394					0.351	0.329		2.148*
Mg2		0.426								0.288			0.358	2.144*
Fe2			0.472				0.526		0.520					3.036*
Fe3				0.473				0.543	0.505					3.042*
P1	1.182	1.365	1.307	1.084										4.938
P2					1.167	1.317	1.272	1.251						5.007
HOH									0.884		0.116			1.000
HW1a					0.188					0.812				1.000
HW1b									0.110	0.890				1.000
HW2a											0.875		0.125	1.000
HW2b	0.264										0.736			1.000
HW3a		0.163										0.837		1.000
HW3b										0.132		0.868		1.000
HW4a						0.225							0.775	1.000
HW4b									0.132				0.868	1.000
$\Sigma_a v$	2.038	1.954	1.841	1.975	2.034	1.936	1.941	1.927	2.019	2.122	2.078	2.034	2.127	

Note: Non-hydrogen bond strengths from Brese and O'Keeffe (1991); hydrogen bond strengths from Ferraris and Ivaldi (1988), based on O-O distances; valence summations are expressed in valence units.
* Cations are each bonded to two of the indicated O atoms.

Figure 5. Edge-sharing $[Fe^{3+}O_2(PO_4)_2]^{7-}$ unit in jahnsite-(NaFeMg).

Hydrogen bonding

The determination of H positions in the current study allows the elucidation of a definitive H-bonding scheme (Table 9) that differs somewhat from that proposed by Moore and Araki. As mentioned above, the M2 octahedra link the slabs in the **c** direction by sharing two of their vertices with P tetrahedra in adjacent slabs. The H-bonds further serve to link the M2 octahedra to the slabs, as well as to one another, and thereby augment the stability of the structure. The bond valence sums for the O atoms (Table 10), with the H-bond contributions considered, are generally well balanced.

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