

# Jahnsite-(CaFeMg), a new mineral from Tom's quarry, South Australia: description and crystal structure

PETER ELLIOTT<sup>1,2,\*</sup>

<sup>1</sup> Department of Earth Sciences, School of Physical Sciences, The University of Adelaide, Adelaide, South Australia 5005, Australia

<sup>2</sup> South Australian Museum, North Terrace, Adelaide, South Australia 5000, Australia

\*Corresponding author, e-mail: peter.elliott@adelaide.edu.au

**Abstract:** Jahnsite-(CaFeMg) is a new member of the whiteite–jahnsite group from Tom's Quarry, Kapunda, South Australia, Australia where it occurs as a low-temperature secondary mineral. Jahnsite-(CaFeMg) forms brownish orange prismatic crystals to 0.2 mm in length. Crystals are transparent, have a vitreous lustre and a good cleavage on {001}. The streak is white. The Mohs hardness is ~4, the tenacity is brittle and the fracture is splintery. The measured density is 2.76(4) g/cm<sup>3</sup> and the calculated density is 2.772 g/cm<sup>3</sup>. Optically jahnsite-(CaFeMg) is biaxial negative with  $\alpha = 1.629(4)$ ,  $\beta = 1.658(4)$ ,  $\gamma = 1.677(4)$  and  $2V_{\text{calc}} = 76.8^\circ$ . Electron-microprobe analyses provided: Na<sub>2</sub>O 0.65, CaO 4.74, Al<sub>2</sub>O<sub>3</sub> 0.06, Fe<sub>2</sub>O<sub>3</sub> 20.18, FeO 9.85, MgO 6.47, MnO 5.02, P<sub>2</sub>O<sub>5</sub> 34.41, H<sub>2</sub>O<sub>calc</sub> 19.46 (from crystal-structure analysis), total 100.84 wt.%. The empirical formula (based on 26 oxygen atoms) is: (Ca<sub>0.70</sub>Na<sub>0.17</sub>Mn<sup>2+</sup><sub>0.16</sub>) $\Sigma$ 1.03Fe<sup>2+</sup><sub>1.00</sub>(Mg<sub>1.33</sub>Mn<sup>2+</sup><sub>0.43</sub>Fe<sup>3+</sup><sub>0.24</sub>) $\Sigma$ 2.00(Fe<sup>3+</sup><sub>1.99</sub>Al<sub>0.01</sub>) $\Sigma$ 2.00(PO<sub>4</sub>)<sub>4.01</sub>(OH)<sub>2.10</sub>H<sub>2</sub>O<sub>7.88</sub>. Jahnsite-(CaFeMg) is monoclinic, *P*2/a, *a* = 14.975(5), *b* = 7.1645(14), *c* = 9.928(2) Å,  $\beta = 110.65(3)^\circ$ , *V* = 996.7(5), Å<sup>3</sup> and *Z* = 2. The eight strongest lines in the powder diffraction pattern are [*d*(Å)(*l*)(*hkl*)]: 9.339(100)(001); 4.923(20)(21–1, 111, 310); 3.562(20)(400); 3.518(20)(112, 40–2); 3.453(20)(202); 2.965(20)(221); 2.839(35)(5-1-1); 2.592(20)(203). The crystal structure has been refined using a single crystal twinned on {001} to *R*1 = 0.0517 on the basis of 1616 observed reflections with *F*<sub>o</sub> > 4 $\sigma$ (*F*<sub>o</sub>) and confirms a whiteite–jahnsite-type structure.

**Key-words:** jahnsite; new mineral; Tom's quarry; Kapunda; crystal structure; phosphate; whiteite–jahnsite group.

## Introduction

Phosphate rock was discovered in the Koonunga Hill area, 10 km E of Kapunda, South Australia, Australia in 1904 (Jack, 1919). Tom's quarry, one of several deposits in the area, has been worked intermittently to the present day. The deposits are low-grade phosphorites derived by leaching of weakly phosphatic limestones or low-grade primary phosphorites during the late Tertiary and the Quaternary (Johns, 1976). The phosphorite in the deposits is highly ferruginous and is overlain by limonitic laterite. Tom's quarry is the largest and most mineralogically diverse of the deposits and collecting over the past 40 years has produced a diverse range of mostly well-crystallized phosphate minerals including cacoxenite, fluellite, leucophosphate, meurigite-Na, minyulite, natrodufrénite–dufrénite, ushkovite, wavellite and xanthoxenite. It is the type locality for peisleyite (Pilkington *et al.*, 1982; Mills *et al.*, 2011) and kapundaite (Mills *et al.*, 2010). A description of the mineralogy of the deposit is provided by Elliott *et al.* (2014).

In 2012, specimens containing prismatic to thin bladed crystals of jahnsite-(NaFeMg) were collected from a

highly weathered goethite-rich area at the eastern end of Tom's Quarry. One specimen, however, contained crystals with a blocky habit and chemical analysis showed these to be a new, CaFeMg member of the jahnsite group. Minerals of the whiteite–jahnsite group have the general formula *X**M**1**M*<sub>2</sub>*M*<sub>3</sub><sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>(OH)<sub>2</sub> · 8H<sub>2</sub>O, where *M*<sub>3</sub> = Fe<sup>3+</sup> and Al (for the jahnsite and whiteite end-members, respectively); *X* = Ca, Na and Mn and the *M*<sub>1</sub> and *M*<sub>2</sub> sites are occupied by Mn, Fe, Mg and Zn. The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2013–111). The holotype specimen is housed in the mineral collection of the South Australian Museum, Adelaide, South Australia (registration number G34045).

## Occurrence

Jahnsite-(CaFeMg) is part of an assemblage of secondary phosphate minerals that have a sedimentary origin. Deposition of secondary phosphates has occurred near

surface at ambient temperatures and has been largely controlled by the availability of cations in groundwaters rather than changes in physical conditions (Segnit *et al.*, 1981). The earliest formed mineral was fluorapatite and the phosphate mineral assemblages have resulted from its breakdown in the presence of acidic Fe- and Al-bearing solutions. Segnit *et al.* (1981) noted that, in general, the Fe-bearing phosphates (beraunite, natrodufrénite–dufrénite and rockbridgeite) were deposited early in the sequence and the alkali-bearing phosphates formed late in the sequence.

### Appearance, physical and optical properties

Jahnsite-(CaFeMg) occurs as blocky to short prismatic crystals lining small cavities and as intergrowths with jahnsite-(NaFeMg) filling veins in a matrix comprising goethite and minor fluorapatite. No other species are directly associated with jahnsite-(CaFeMg) but other cavities on the type specimen contain crystals of natrodufrénite. Individual crystals of jahnsite-(CaFeMg) are up to 0.2 mm in length and 0.15 mm across. The mineral is brownish orange, the streak is white, crystals are transparent and the lustre is vitreous. It has a Mohs hardness of ~4 and a good {001} cleavage. Tenacity is brittle and the fracture is splintery.

The mineral shows no fluorescence, either under SW or LW ultraviolet radiations. The density, measured using the sink-float method in a sodium polytungstate–water mixture, is 2.76(4) g/cm<sup>3</sup>, which compares well with the value of 2.772 g/cm<sup>3</sup> calculated from the empirical formula and the unit-cell dimensions derived from the crystal-structure analysis.

Jahnsite-(CaFeMg) is biaxial negative, with  $\alpha$  1.629(4),  $\beta$  1.658(4),  $\gamma$  1.677(4). As an interference figure was not able to be obtained  $2V$  was not measured, but  $2V_{\text{calc}} =$

76.8°; no dispersion was noted. Pleochroism is weak;  $X$  very pale grey,  $Y$  orange-pink,  $Z$  pale orange; absorption  $Y > Z > X$ . A Gladstone-Dale calculation gave a compatibility index of 0.021, which is classed as excellent (Mandarino, 1981).

### Chemical composition

Chemical analyses were carried out using a Cameca SXFive electron microprobe (energy-dispersive spectroscopy mode, 20 kV, 20 nA and 5  $\mu\text{m}$  beam diameter). The following standards and X-ray lines were used: albite (NaK $\alpha$ ), wollastonite (CaK $\alpha$ ), almandine (FeK $\alpha$ , MgK $\alpha$ , AlK $\alpha$ ), rhodonite (MnK $\alpha$ ), and hydroxylapatite (PK $\alpha$ ). No additional element with atomic number  $\geq 9$  was detected in amounts  $>0.05$  wt% oxide. Data were processed using the  $\varphi(\rho z)$  correction procedure of Pouchou & Pichoir (1985). One individual crystal and two grains of vein material were analysed. As is common with whiteite–jahnsite minerals, which frequently show pronounced compositional zonation (Kampf *et al.*, 2008; Grey *et al.*, 2010; Yakovenchuk *et al.*, 2012), the vein material comprises two compositional zones; jahnsite-(CaFeMg) and jahnsite-(NaFeMg) with a ratio of ~1:1 and with a sharp interface between the zones, as shown by backscattered-electron (BSE) images. The analysed crystal showed no evidence of chemical zoning and comprised only jahnsite-(CaFeMg). Analytical data for the crystal are given in Table 1. The empirical formula unit, based on 26 oxygen atoms per formula unit (pfu) and with site assignments using the approach of Moore & Ito (1978) for whiteite–jahnsite-group minerals is  $(\text{Ca}_{0.70}\text{Na}_{0.17}\text{Mn}^{2+}_{0.16})_{\Sigma 1.03}\text{Fe}^{2+}_{1.00}(\text{Mg}_{1.33}\text{Mn}^{2+}_{0.43}\text{Fe}^{3+}_{0.24})_{\Sigma 2.00}(\text{Fe}^{3+}_{1.99}\text{Al}_{0.01})_{\Sigma 2.00}(\text{PO}_4)_{4.01}(\text{OH})_{2.10}\text{H}_2\text{O}_{7.88}$ .

### X-ray powder diffraction data

Powder X-ray diffraction (Table 2) data were collected using a Rigaku Hiflux Homelab diffractometer (CuK $\alpha$  X-radiation,  $\lambda = 1.541870$  Å). Intensities were visually estimated and the calculated intensities were obtained from the structural model. Unit-cell parameters refined using the Le Bail profile-fitting method (Le Bail *et al.*, 1988; Hunter, 1998) starting from the unit-cell parameters determined from single-crystal techniques are  $a = 14.985(2)$ ,  $b = 7.150(1)$ ,  $c = 9.877(2)$  Å,  $\beta = 110.583(3)^\circ$ ,  $V = 990.8(2)$  Å<sup>3</sup>.

### Crystal structure

A crystal of jahnsite-(CaFeMg),  $0.06 \times 0.035 \times 0.03$  mm in size, was attached to a glass fibre and mounted on an Oxford Diffraction Xcalibur E diffractometer equipped with an Eos CCD detector. Intensity

Table 1. Compositional data for jahnsite-(CaFeMg).

Constituent	Wt.%	Range	Standard deviation
Na <sub>2</sub> O	0.65	0.20–1.23	0.36
CaO	4.74	3.67–6.19	0.85
Al <sub>2</sub> O <sub>3</sub>	0.06	0.00–0.20	0.05
Fe <sub>2</sub> O <sub>3</sub> *	20.18	18.82–23.36	1.35
FeO*	9.85	5.87–12.52	2.21
MgO	6.47	5.73–7.63	0.48
MnO	5.02	4.08–5.55	0.37
P <sub>2</sub> O <sub>5</sub>	34.41	33.27–36.16	0.85
H <sub>2</sub> O**	19.46		
Total	100.84		

Note: Number of analysis = 17.

\*Fe<sub>2</sub>O<sub>3</sub> and FeO contents are calculated assuming that the M2 site is occupied by Mg, Mn and Fe<sup>3+</sup> and the M3 site is occupied by Fe<sup>3+</sup> and Al.

\*\*H<sub>2</sub>O calculated from the crystal structure analysis.

Table 2. X-ray powder diffraction data for jahnsite-(CaFeMg).

$I_{\text{obs}}$	$d_{\text{obs}}$	$I_{\text{calc}}$	$d_{\text{calc}}$	$h$	$k$	$l$	
100	9.339	100	9.290	0	0	1	
5	7.070	4	7.165	0	1	0	
5	6.380	4	6.379	1	1	0	
10	5.699	21	5.704	1	-1	-1	
20	4.923	{	4	4.963	2	1	-1
			23	4.904	1	1	1
5	4.812	4	4.834	2	0	1	
10	4.666	4	4.645	0	0	2	
15	4.094	5	4.080	1	-1	-2	
10	3.931	{	4	3.937	2	-1	-2
			4	3.913	3	1	0
5	3.745	10	3.743	0	2	0	
20	3.562	39	3.555	4	0	0	
20	3.518	{	4	3.503	1	1	2
			4	3.497	4	0	-2
20	3.453	4	3.440	2	0	2	
5	3.346	4	3.364	1	2	-1	
10	3.290	4	3.294	3	1	1	
15	3.279	20	3.276	2	2	0	
5	3.182	4	3.178	1	2	1	
	3.108	4	3.097	2	1	2	
20	2.965	12	2.952	2	2	1	
15	2.886	7	2.878	4	0	-3	
35	2.839	44	2.837	5	-1	-1	
5	2.626	6	2.625	5	1	0	
20	2.592	21	2.588	2	0	3	
5	2.492	8	2.482	2	0	-4	
5	2.426	{	6	2.427	2	-2	-3
			6	2.418	4	0	2
5	2.354	4	2.356	2	-1	-4	
5	2.333	4	2.330	0	0	4	
		4	2.052	6	0	-4	
		4	2.025	1	-2	-4	
5	1.999	6	1.997	2	0	-5	
	1.971	16	1.968	7	1	-3	
5	1.953	{	5	1.951	0	2	4
			9	1.949	2	3	2
			4	1.947	2	-3	-3
10	1.922	9	1.911	2	-1	-5	
5	1.877	20	1.871	5	3	-1	
5	1.821	18	1.823	7	2	-1	

Note: Observed intensities estimated visually. Calculated intensities were obtained using the program LAZY PULVERIX (Yvon *et al.*, 1977); only reflections with  $I_{\text{calc}} > 4$  were considered.

data were collected at room temperature using MoK $\alpha$  X-radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a detector distance of 46.43 mm. The data collection and processing conditions are summarized in Table 3. Unit-cell dimensions were determined by least-squares refinement of 857 reflections in the  $\theta$  range 2.84–28.84° and are given in Table 3, together with information pertaining to data collection and structure refinement. The data were processed using the CrysAlisPro program (Oxford Diffraction, 2009) and corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm, as implemented in CrysAlisPro. Structure refinement was

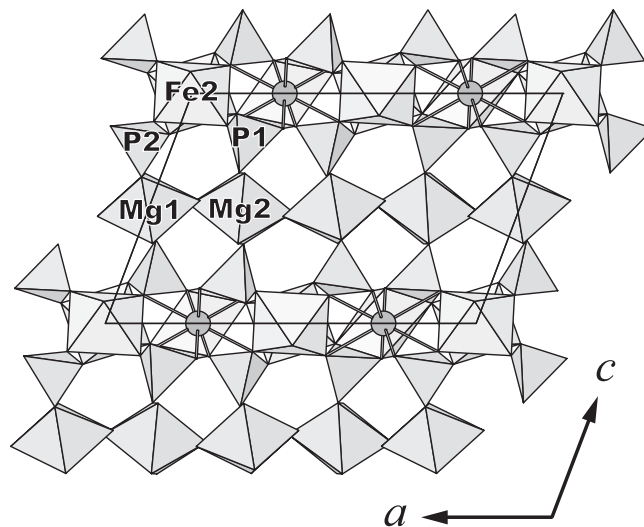


Fig. 1. The crystal structure of jahnsite-(CaFeMg) viewed along [010]. The X site is shown as grey circles. The unit cell is outlined. All structure drawings were completed using ATOMS (Shape Software, 1997).

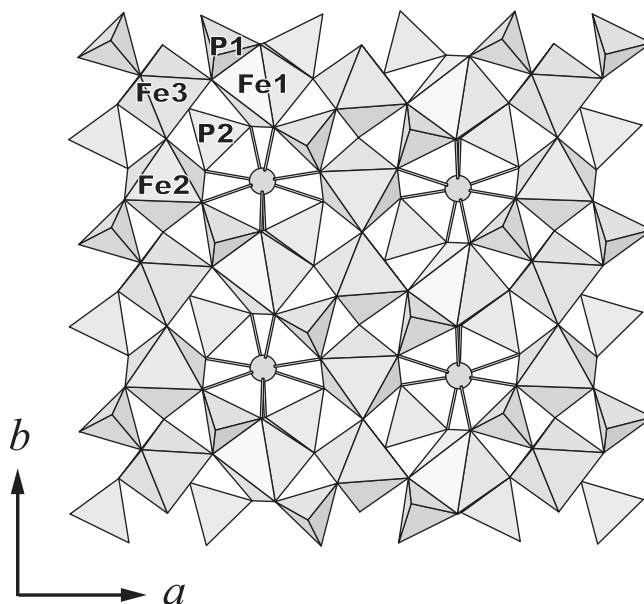


Fig. 2. The crystal structure of jahnsite-(CaFeMg) viewed perpendicular to (001). The X site is shown as grey circles.

initiated in space group  $P2_1/a$  using the coordinates of Moore & Araki (1974) and refined using SHELXL-97 (Sheldrick, 2008). The  $R$  index converged to a value of 5.45 % for a model including anisotropic displacement parameters for all atoms. Crystals of whiteite–jahnsite group minerals are invariably twinned on (001) and the twin matrix  $[1 \ 0 \ 0/0 \ -1 \ 0/-0.468 \ 0 \ -1]$  was confirmed using ROTAX in the WinGX suite of programs (Farrugia, 1999). A SHELX HKLF 5 reflection file was created and refinement resulted in refined twin

Table 3. Crystal data, data collection and refinement details.

Crystal data	
Space group	<i>P2/a</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.975(5), 7.1645(14), 9.928(2)
<i>V</i> (Å <sup>3</sup> ), <i>Z</i>	996.7(5), 2
<i>F</i> (000)	953.0
$\mu$ (mm <sup>-1</sup> )	3.02
Absorption correction	multi-scan, $T_{\min}$ , $T_{\max}$ = 0.70, 1.00
Crystal dimensions (mm)	0.06 × 0.035 × 0.03
Data collection	
Diffractometer	Oxford Diffraction Xcalibur E
Temperature (K)	293
Radiation	MoK $\alpha$ , $\lambda$ = 0.71073 Å
Crystal detector distance (mm)	46.43
Rotation axis, width (°)	$\omega$ , 2.0
Total number of frames	231
Collection time per degree (s)	100
$\theta$ range (°)	2.84–28.90
<i>h</i> , <i>k</i> , <i>l</i> ranges	–18 → 18, –4 → 9, –11 → 13
Total reflections measured	4300
Unique reflections	4300 ( $R_{\text{int}}$ = 0.0581)
Refinement	
Refinement on	$F^2$
$R1^*$ for $F_0 > 4\sigma(F_0)$	5.17 %
$wR2^\dagger$ for all $F_0^2$	13.41 %
Reflections used $F_0^2 > 4\sigma(F_0^2)$	1616
Number of parameters refined	178
Goof	0.635
$(\Delta/\sigma)_{\text{max}}$	0.000
$\Delta P_{\text{max}}$ , $\Delta P_{\text{min}}$ (e/Å)	1.519, –0.628

components of 0.08:0.92 and  $R1 = 5.17\%$ . The positions of H atoms could not be located in difference-Fourier maps. Refined coordinates and anisotropic-displacement factors are listed in Table 4, selected interatomic distances are given in Table 5, and a bond-valence table is shown as Table 6.

Chains of corner-sharing *M3* octahedra (Fe2 and Fe3) which are decorated by bridging  $\text{P1O}_4$  and  $\text{P2O}_4$  groups extend in the *b*-direction (Figs. 1 and 2). The chains are linked in the *a*-direction by *X* polyhedra, forming slabs parallel to (100). The Fe1 (*M1*) octahedron shares edges with two  $\text{P1O}_4$  tetrahedra. Slabs link in the *c*-direction via Mg (*M2*) octahedra which share corners with  $\text{P1O}_4$  and  $\text{P2O}_4$  tetrahedra and by hydrogen bonding.

The *X* site is coordinated by eight  $\text{O}^{2-}$  anions to form a distorted square antiprism. The *X*–O distances are very similar to those observed in the structures of jahnsite-(NaFeMg) (Kampf *et al.*, 2008) and jahnsite-(CaMnMg) (Moore & Araki, 1974), with four *X*–O bond distances in the range 2.37–2.50 Å and two longer *X*–O bond distances at 2.78 Å. The mean bond distance for the *X* site confirms occupancy by predominantly large cations and the observed site-scattering, 18.20(8) electrons, is consistent with the population of  $\text{Ca}_{0.70}\text{Na}_{0.17}\text{Fe}^{2+}_{0.13}$  from the chemical analysis. The valence sum is significantly less than 2.0 (Table 3) in agreement with partial occupancy by Na.

The assignments of Mg to the *M2* sites (Mg1 and Mg2),  $\text{Fe}^{2+}$  to the Fe1 site and  $\text{Fe}^{3+}$  to the *M3* sites

Table 4. Fractional atomic coordinates and displacement parameters for jahnsite-(CaFeMg).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ca ( <i>X</i> )	0.25	0.9784(4)	0	0.0206(10)	0.0202(17)	0.0084(15)	0.027(2)	0	0.0000(14)	0
Fe1 ( <i>M1</i> )	0.25	0.4786(2)	0	0.0125(6)	0.0108(9)	0.0117(10)	0.0177(11)	0	0.0084(8)	0
Mg1 ( <i>M2</i> )	0.5	0	0.5	0.0180(8)	0.0214(13)	0.0072(12)	0.0158(15)	–0.0071(11)	–0.0052(11)	0.0012(10)
Mg2 ( <i>M2</i> )	0.25	0.5036(4)	0.5	0.0073(9)	0.0067(14)	0.0091(15)	0.0060(17)	0	0.0020(12)	0
Fe2 ( <i>M3</i> )	0	0	0	0.0087(5)	0.0083(8)	0.0017(8)	0.0169(10)	0.0001(7)	0.0055(7)	0.0000(6)
Fe3 ( <i>M3</i> )	0	0.5	0	0.0077(5)	0.0062(8)	0.0044(8)	0.0127(10)	0.0032(7)	0.0037(7)	–0.0006(6)
P1	0.18729(11)	0.2655(3)	0.1889(2)	0.0075(6)	0.0031(9)	0.0060(10)	0.0116(11)	–0.0041(10)	0.0003(7)	0.0026(9)
P2	0.08120(12)	0.7470(3)	0.7967(2)	0.0079(5)	0.0058(8)	0.0068(10)	0.0110(10)	–0.0009(9)	0.0028(7)	0.0025(9)
O1	0.2806(3)	0.2437(7)	0.1523(5)	0.0307(13)	0.019(2)	0.041(3)	0.036(3)	–0.005(3)	0.014(2)	0.009(3)
O2	0.2081(3)	0.3019(7)	0.3451(5)	0.0277(14)	0.031(3)	0.028(3)	0.026(3)	0.000(3)	0.012(3)	0.000(2)
O3	0.1275(3)	0.0887(6)	0.1404(6)	0.0315(15)	0.022(3)	0.009(2)	0.047(4)	–0.010(3)	–0.010(3)	0.002(2)
O4	0.1408(3)	0.4339(6)	0.0884(5)	0.0231(14)	0.014(3)	0.019(3)	0.036(4)	0.002(3)	0.009(2)	0.007(2)
O5	0.1871(3)	0.6887(7)	0.8578(5)	0.0308(15)	0.012(2)	0.047(4)	0.030(3)	0.002(3)	0.003(2)	0.005(2)
O6	0.0513(3)	0.7832(6)	0.6364(5)	0.0261(13)	0.034(3)	0.019(3)	0.029(3)	0.008(3)	0.015(3)	0.001(2)
O7	0.0746(3)	0.9269(6)	0.8776(5)	0.0222(13)	0.028(3)	0.015(2)	0.029(3)	–0.008(2)	0.017(3)	0.002(2)
O8	0.0196(3)	0.5914(6)	0.8221(6)	0.0284(14)	0.029(3)	0.022(3)	0.042(4)	–0.004(3)	0.022(3)	0.003(2)
OH	0.0268(3)	0.7493(6)	0.0962(5)	0.0166(11)	0.010(2)	0.012(2)	0.026(3)	–0.001(3)	0.0045(19)	0.000(2)
OW1	0.2231(4)	0.7227(7)	0.3467(6)	0.0402(15)	0.051(4)	0.028(3)	0.041(4)	–0.005(3)	0.015(3)	0.009(3)
OW2	0.4542(4)	0.2086(6)	0.3475(6)	0.0392(16)	0.054(4)	0.022(3)	0.023(3)	0.011(3)	–0.008(3)	–0.007(3)
OW3	0.6301(3)	0.9921(7)	0.4654(6)	0.0400(16)	0.024(3)	0.043(4)	0.055(4)	–0.011(4)	0.017(3)	–0.010(3)
OW4	0.3936(3)	0.5124(7)	0.5170(5)	0.0345(16)	0.030(3)	0.032(3)	0.045(4)	0.010(3)	0.018(3)	0.002(3)

Table 5. Selected interatomic distances (Å) and possible hydrogen bonds for jahnsite-(CaFeMg).

Ca	O1	2.371(5) × 2	Fe2	O7	1.989(4) × 2
	O5	2.500(5) × 2		OH	2.007(4) × 2
	O7	2.502(4) × 2		O3	2.029(4) × 2
	O3	2.782(5) × 2		<Fe-O>	2.008
<Ca-O>		2.539			
Fe1	O5	2.052(5) × 2	Fe3	OH	1.998(4) × 2
	O4	2.135(4) × 2		O8	2.000(5) × 2
	O1	2.200(5) × 2		O4	2.033(4) × 2
	<Fe-O>	2.129		<Fe-O>	2.010
Mg1	O6	2.025(4) × 2	P1	O2	1.493(5)
	OW2	2.065(5) × 2		O3	1.528(4)
	OW3	2.094(5) × 2		O1	1.564(5)
	<Mg-O>	2.061		O4	1.571(4)
<Mg-O>		2.061	<P-O>		1.539
Mg2	O2	2.041(6) × 2	P2	O6	1.516(5)
	OW4	2.098(5) × 2		O8	1.524(5)
	OW1	2.123(6) × 2		O5	1.540(5)
	<Mg-O>	2.087		O7	1.542(4)
<Mg-O>		2.087	<P-O>		1.531

Possible hydrogen bonds			
OH-H1...OW2	3.068	OW3-H6...OW1	2.94
OW1-H2...O5	2.814	OW3-H7...O2	2.866
OW1-H3...OH	3.116	OW4-H8...O6	2.766
OW2-H4...OW4	3.078	OW4-H9...O8	3.042
OW2-H5...O1	2.650		

(Fe2 and Fe3) is borne out by the bond lengths and valence balance sums. Site-scattering values for the Mg1 and Mg2 sites, 18.63(6) electrons and 14.60(6) electrons respectively, suggests greater presence of Fe<sup>3+</sup> and Mn<sup>2+</sup> at the Mg1 site. The mean bond distance for the M1 site, 2.129 Å, is greater than the corresponding value for jahnsite-(NaFeMg) of 2.049 Å (Kampf *et al.*, 2008), consistent with occupancy of the site by Fe<sup>2+</sup> rather than Fe<sup>3+</sup> as in jahnsite-(NaFeMg). The valence sums for the M2 sites (Mg1 and Mg2) are greater than 2.0 suggesting the possibility of some occupancy of these sites by trivalent cations.

Although the H atoms associated with the OH and H<sub>2</sub>O groups could not be located, stereochemistry and incident bond-valence requirements indicate that the hydrogen bond scheme (Table 5) would be expected to be identical to that in jahnsite-(NaFeMg) (Kampf *et al.*, 2008). Hydrogen bonds are directed towards undersaturated anions O1, O2, O5, O6 and O8 as well as OW1, OW2 and OW4.

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Table 6. Bond-valence analysis for jahnsite-(CaFeMg).

	Ca	Fe1	Mg1	Mg2	Fe2	Fe3	P1	P2	H1	H2	H3	H4	H5	H6	H7	H8	H9	Sum excluding H	Sum including H
O1	0.314 x <sup>2</sup> ↓	0.279 x <sup>2</sup> ↓					1.139						0.22					1.73	1.95
O2				0.440 x <sup>2</sup> ↓	0.475 x <sup>2</sup> ↓		1.372								0.15			1.81	1.96
O3	0.095 x <sup>2</sup> ↓						1.272											1.85	1.85
O4		0.332 x <sup>2</sup> ↓					1.129											1.94	1.94
O5	0.205 x <sup>2</sup> ↓	0.423 x <sup>2</sup> ↓						1.241		0.17								1.87	2.04
O6			0.445 x <sup>2</sup> ↓					1.317								0.19		1.77	1.96
O7	0.207 x <sup>2</sup> ↓							1.241										1.98	1.98
O8					0.532 x <sup>2</sup> ↓			1.300									0.10	1.82	1.92
OH					0.511 x <sup>2</sup> ↓				0.91		0.05							1.04	2.00
OW1				0.350 x <sup>2</sup> ↓						0.83	0.95							0.35	2.25
OW2		0.400 x <sup>2</sup> ↓							0.09			0.90	0.78					0.40	2.17
OW3		0.377 x <sup>2</sup> ↓																0.38	2.11
OW4				0.385 x <sup>2</sup> ↓								0.10						0.39	2.20
Sum	1.642	2.068	2.444	2.350	3.034	3.051	4.912	5.099	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.81	0.90

Note: Non-hydrogen bond strengths from Bressé & O'Keefe (1991); hydrogen bond strengths from Brown & Altermatt (1985), based on O-O distances. Bond-valences for the Ca, Fe1, Mg1, Mg2, Fe2 and Fe3 site are based on occupancies derived from the chemical analysis.

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