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Crystal chemistry of macfallite: Relationships to sursassite and pumpellyite

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ABSTRACT

The crystal chemistry of macfallite from Keweenaw County, Michigan was studied using electron microprobe, thermogravimetry (TG), differential thermal analysis (DTA), powder Fourier transform infrared (FTIR) spectroscopy, and single-crystal X-ray diffraction methods. The chemical formula derived from the electron-microprobe measurements is

$$(\mathrm{Ca}_{2.03}\mathrm{Na}_{0.01})_{\Sigma 2.04}(\mathrm{Mn}^{3+}_{2.51}\mathrm{Al}_{0.27}\mathrm{Mg}_{0.09}\mathrm{Cu}^{2+}_{0.03}\mathrm{V}^{3+}_{0.01})_{\Sigma 2.91}\mathrm{Si}_{3.05}\mathrm{O}_{10.88}(\mathrm{OH})_{3.12}\ (Z = 2).$$

An analysis using the intensities of the Mn$L\beta$ and Mn$L\alpha$ X-ray lines shows that most Mn is trivalent. The weight loss from TG measurement is 7.7 wt% at 1000 °C, most of which is interpreted to be due to the loss of structural OH groups. The crystal structure of macfallite [a = 8.959(3), b = 6.072(2), c = 10.218(4) Å, β = 110.75(3)°, space group $P2_1/m$], which is isostructural with sursassite, was refined using 1717 unique reflections to R = 4.1%. The site populations at the three independent octahedral sites, Mn1, Mn2, and Mn3, are $\mathrm{Mn}_{0.82}\mathrm{Al}_{0.06}\mathrm{Mg}_{0.09}\mathrm{Cu}_{0.03}$, $\mathrm{Mn}_{0.75}\mathrm{Al}_{0.25}$, and $\mathrm{Mn}_{0.95}\mathrm{Al}_{0.05}$, respectively. In agreement with a bond-valence analysis, three crystal-chemically different OH groups are located at the O6, O10, and O11 positions. The site O7 is mostly occupied by oxygen, but minor amounts of hydroxyl may be located there as well. The powder FTIR spectrum in the region of the OH-stretching vibrations is characterized by three strong bands at 3413, 3376, and 3239 cm^{-1} and an additional broad absorption band around 2900 cm^{-1}. The latter results from a relatively strong hydrogen bond, O6-H···O11, with a length of ~2.63 Å. Although there are three main hydroxyl groups occurring in macfallite, the exact number depends on the concentration of trivalent and divalent cations at the Mn1 site. If divalent cations occur at Mn1, a fourth OH group is necessary to maintain charge balance.

Keywords: Macfallite, pumpellyite, sursassite, Mn silicates, hydrous silicates, FTIR spectroscopy, crystal structure

INTRODUCTION

Low-temperature silicates, many of which are hydrous, are often complex both structurally and compositionally. They often occur as fine-grained aggregates, and it is difficult to obtain good single crystals and/or sufficient amounts of material for experimental investigation. Macfallite is such a relatively low-temperature hydrous silicate with the ideal formula $\mathrm{Ca_2Mn^{3+}_3Si_3O_{11}(OH)_3}$. It has been reported from three localities: (1) fissures and lenses in Keweenaw basalt near Manganese Lake, Copper Harbor, Keweenaw County, Michigan (Moore et al. 1979); (2) metamorphosed and metasomatized manganese deposits in metacherts from the Cerchiara mine, eastern Liguria, Italy (Basso et al. 1989); and (3) low-grade metamorphic rocks from the Wakasa manganese mine, Hokkaido, Japan (Miyajima et al. 1998).

The crystal structure of macfallite was first determined by Moore et al. (1985) who proposed the general structural formula $\mathrm{Ca1Ca2Mn1Mn2Mn3}Z_3\mathrm{O_{11}(OH)_3}$, where Ca1 and Ca2 represent seven coordinated sites, Mn1, Mn2, and Mn3, octahedral sites, and Z, tetrahedral sites. However, the original structure determination (R = 18.4%) allowed only a description of the average crystal structure and not an examination of detailed crystal-chemical properties. Although little is known about the compositional variations in natural crystals, macfallite is compositionally similar to okhotskite (Mn^{3+}-analog of pumpellyite) of composition $\mathrm{Ca_8(Mn^{2+},Mg)_4(Mn^{3+},Al,Fe^{3+})_8Si_{12}O_{56-n}(OH)_n}$ (Togari and Akasaka 1987). A polysomatic description for isostructural macfallite and sursassite, as well as pumpellyite, ardenite and lawsonite, the so-called 6 × 9 Å structures with corresponding axial translations, was presented by Moore et al. (1985) and Ferraris et al. (1986).

In this study, we investigated, further and in detail, the crystal structure and crystal-chemical properties of macfallite. The following experimental methods were used: electron microprobe analysis, thermogravimetry (TG), differential thermal analysis (DTA), powder Fourier transform infrared spectroscopy (FTIR), and single-crystal X-ray diffraction. A bond-valence analysis was also carried out. Finally, we examined the structural and compositional relationships between macfallite, pumpellyite, and sursassite including the nature of their H-bonding systems.

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EXPERIMENTAL METHODS

Specimen

The studied sample was collected from veinlets including macfallite, calcite, orientite, and braunite that occur in basalt located near Manganese Lake, Copper Harbor, in Keweenaw County, Michigan (Moore et al. 1979). Macfallite occurs as needle- and prism-like crystals that are elongated along the *b* axis and are up to 3 mm in length. The crystals are dark reddish-brown, and are pleochroic from reddish brown to yellow in polarized light. Crystals are frequently twinned with {001} as a twin plane.

Chemical analysis

The chemical composition of macfallite was determined using a JEOL JXA-8900R electron probe microanalyzer at the University of Kiel. The abundances of Si, Ti, Al, Cr, V, Fe, Mn, Cu, Mg, Ca, Sr, Ba, K, and Na were measured using an accelerating voltage of 20 kV and a beam current of 20 nA, with a beam diameter of 1 μm. The following standards were used: wollastonite (Si), rutile (Ti), anorthite (Al, Ca), chromite (Cr), vanadium metal (V), fayalite (Fe), rhodonite (Mn), elemental copper (Cu), forsterite (Mg), a Ge-Al-Ca glass containing 10 wt% Sr (Sr), a Si-Al-Ca glass containing 10 wt% Ba (Ba), natural microcline (K), and anorthoclase (Na). The PRZ method (modified ZAF) was used for data correction for all elements.

Semi-quantitative Mn^{2+}/Mn^{3+} ratios in macfallite were determined using the ratio of the X-ray intensities of the Mn$L\beta$ and Mn$L\alpha$ lines, following the methods of Albee and Chodos (1970) and Kimura and Akasaka (1999). The X-ray intensities of the Mn$L\beta$ and Mn$L\alpha$ lines were measured using a JEOL JXA-8800M electron-probe microanalyzer at Shimane University, Japan. The measurements were done using an accelerating voltage of 15 kV, a beam current of 30 nA and beam diameter of 10 μm. Emission spectra of the Mn$L\beta$ and Mn$L\alpha$ lines were measured using a TAP monochromator crystal for a range of *L*-values between 206 and 213 mm with a step interval of 0.05 mm and a step counting time of 10 s. The *L* values are the distances (in millimeters) between the measuring spot on the sample and the point on the monochromator crystal where the X-ray beam impinges, and are related through the equation $L = (R/d) \times n\lambda$ to the wavelength of X-rays (λ in Å), the radius of the Roland circle ($R = 140$ mm for the JEOL JXA-8800M), the (001) *d*-spacings (Å) of the monochromator crystal and the order of Bragg reflection (n). The measured spectra were fitted with Lorentzian curves by least-squares methods to determine peak positions, peak widths, and peak intensities using a program written by Kimura and Akasaka (1999). The equation, $I(\mathrm{Mn}L\beta)/I(\mathrm{Mn}L\alpha) = 0.46 \times \mathrm{Mn}^{2+}/(\mathrm{Mn}^{2+} + \mathrm{Mn}^{3+}) + 0.554$ (Kimura and Akasaka 1999), where I represents intensity, was employed for the estimation of the Mn^{2+}/Mn^{3+} ratio.

DTA/TG measurement

DTA/TG measurements were carried using a SHIMADZU DTG-60H instrument on 17.15 mg of material from room temperature to 1000 °C under a flow of N_2 gas with a heating rate of 10 °C/min.

FTIR spectroscopy

The powder FTIR spectrum was measured with a BRUKER IFSS/66v FTIR spectrometer, using the KBr pellet technique, in the wave region between 4000 and 350 cm^{-1}. A pellet of 13 mm diameter was prepared by pressing a mixture of 1 mg of powdered macfallite and 200 mg of dried KBr under vacuum. The pellet was kept in a vacuum desiccator for 24 h at 150 °C to minimize adsorbed water. The spectrum was recorded under vacuum at a resolution of 2 cm^{-1} by combining 512 scans. Spectral analysis, including baseline adjustment and peak fitting, was performed using the OPUS software package (Bruker).

Single-crystal structure analysis

X-ray diffraction data for a single crystal of macfallite were collected using a STOE STADI4 four-circle diffractometer. A prismatic crystal of size 0.32 × 0.07 × 0.06 mm was mounted on a glass fiber and intensity data were measured at room temperature using graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The reflection statistics and systematic absences were consistent with space groups $P2_1$ and $P2_1/m$. Subsequent attempts to solve the structure indicated that the observed average structure is centrosymmetric and for this reason $P2_1/m$ is the correct space group. Structure refinement was performed using the SHELXL-97 program (Sheldrick 1997). Scattering factors for neutral atoms were employed. Positions of the hydrogen atoms of the hydroxyl groups were derived from difference Fourier synthesis. Subsequently, hydrogen positions were refined assuming full occupancy at a fixed value of $U_{iso} = 0.05$ Å^2. The site populations for the Ca1, Ca2, Mn1, Mn2, and Mn3 were determined in accord with Hawthorne et al. (1995). The hydrogen positions were refined with a bond distance constraint of O-H = 0.98 Å (Franks 1973). Atom labeling, except for H sites, follows the nomenclature for iso-structural sursassite (Mellini et al. 1984).

RESULTS

Chemical composition of macfallite

Macfallite crystals typically show compositional zoning with Al-rich cores and Mn-rich rims, and the total Mn_2O_3 concentration varies between 28.0 and 39.4 wt%. The average chemical composition of our macfallite sample, based on 46 point analyses, is given in Table 1. The corresponding crystal-chemical formula is

$$(Ca_{2.03}Na_{0.01})_{\Sigma 2.04}(Mn^{3+}_{2.51}Al_{0.27}Mg_{0.09}Cu^{2+}_{0.03}V^{3+}_{0.01})_{\Sigma 2.91}Si_{3.05}O_{10.88}(OH)_{3.12}$$

where the total number of cations, except H ions, was normalized to 8 and the amount of OH was calculated using charge balance considerations. The macfallite crystal used for the X-ray single-crystal refinement is from the same hand specimen, and the average chemical composition in Table 1 was, therefore, used to constrain Mg and Cu contents in the site population refinement.

DTA/TG measurement

The DTA/TG results are shown in Figure 1. The TG trace shows weight loss starting around 500 °C. The measured weight loss for the sample at the final temperature of 1000 °C corresponds to 7.7 wt%, most of which is related to structural OH groups. The TG results indicate that no loosely held molecular H_2O is present in macfallite. The change in the DTA signal starting around 300 °C is mainly related to increased atomic vibrations, much of it related to the OH groups followed by eventual dehydroxylation of the structure. At roughly 750 °C, the macfallite structure breaks down and various solid-state reactions begin to occur.

Infrared spectrum

The FTIR powder spectrum between 4000 and 1500 cm^{-1} is shown in Figure 2. The strongest absorption bands are located in the range between 3600 and 2700 cm^{-1}. Three intense bands at 3413, 3376, and 3239 cm^{-1} and an additional broad absorption feature at about 2900 cm^{-1} were assigned to OH vibrations.

TABLE 1. Composition of macfallite based on 46 point analyses

Oxide	wt%	s.d.	Element	apfu*	s.d.
SiO_2	33.14	0.41	Si	3.05	0.03
Al_2O_3	2.49	1.74	Al	0.27	0.18
V_2O_3†	0.09	0.09	V^{3+}	0.01	0.01
Fe_2O_3†	0.05	0.02	Fe^{3+}	0.00	0.00
Mn_2O_3†	35.80	2.96	Mn^{3+}	2.51	0.23
CuO†	0.45	0.31	Cu^{2+}	0.03	0.02
MgO	0.69	0.51	Mg	0.09	0.07
CaO	20.53	0.31	Ca	2.03	0.02
SrO	0.07	0.01	Sr	0.00	0.00
Na_2O	0.03	0.02	Na	0.01	0.00
Total	93.34			8.00	

* Total cations = 8.

† Total V, Fe, Mn, and Cu as V_2O_3, Fe_2O_3, Mn_2O_3, and CuO, respectively.

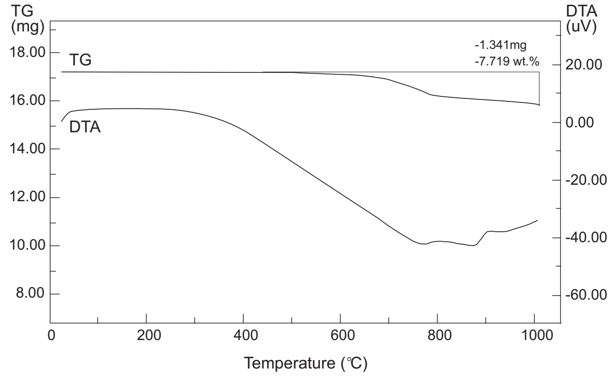

FIGURE 1. DTA and TGA results on macfallite.

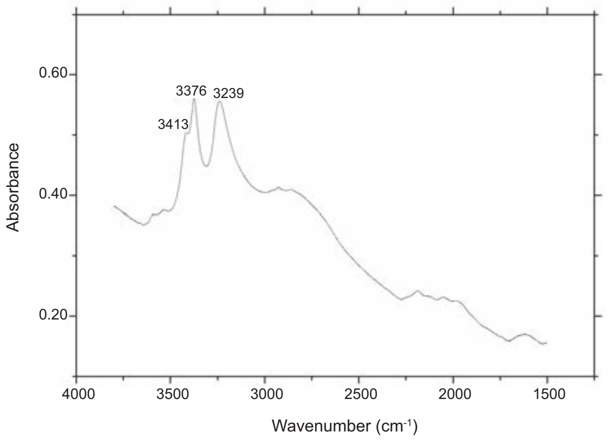

FIGURE 2. Powder infrared spectrum of macfallite between 4000 and 1500 cm^{-1}.

Crystal structural solution and refinements

Crystallographic data and refinement parameters are summarized in Table 2. The refined atomic positions and anisotropic displacement parameters are listed in Table 3. Interatomic distances and angles are listed in Table 4. Table 5 gives the site-scattering values and cation assignments. The crystal structure of macfallite is shown in Figure 3.

Both electron-microprobe data and the site-scattering values indicate that the Ca1 and Ca2 sites are occupied only by Ca. The site populations for Mn^{3+} and Al at the Mn1, Mn2, and Mn3 sites were calculated by use of the following procedure: (1) elements with less than 0.01 atoms per formula unit (apfu) were omitted;

TABLE 2. Crystallographic data for macfallite and experimental details for the single-crystal X-ray diffraction analysis

Crystal size (mm)		0.32 x 0.07 x 0.06
Space group		$P2_1/m$
Cell parameters	a (Å)	8.959(3)
	b (Å)	6.072(2)
	c (Å)	10.218(4)
	β (°)	110.75(3)
	V (Å^3)	519.8(6)
D_{calc} (g/cm^3)		3.454
Radiation		Mo$K\alpha$
Monochrometer		Graphite
Diffractometer		STOE STADI4
Scan type		ω scans
θ_{min}(°)		2.10
θ_{max}(°)		30.50
Absorption coefficient μ (mm^{-1})		5.013
Collected reflections		3485
Unique reflections		1717
R_{int} (%)		8.00
Index limits		$-12 \le h \le 11, -8 \le k \le 8, 0 \le l \le 14$
Refinement system used		SHELXL-97 (Sheldrick 1997)
Refinement on		F^2
R_1 (%)		4.12
wR_2 (%)		9.41
No. of parameters		136
Weighting scheme		$\omega = 1/[\sigma^2(F_o^2) + (0.0490P)^2]$ where $P = [\mathrm{MAX}(F_o^2, 0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max}$		0.00
$\Delta\rho_{max}$ (e Å^{-3})		0.958
$\Delta\rho_{min}$ (e Å^{-3})		−0.913

TABLE 3. Refined atomic positions, isotropic, and anisotropic displacement parameters

Site	neq*	W†	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}
Ca1	2	*e*	0.1670(1)	1/4	0.3134(1)	0.0076(4)	0.0116(5)	0.0084(4)	0	0.0018(3)	0	0.0095(3)
Ca2	2	*e*	0.2949(1)	1/4	0.6813(1)	0.0119(4)	0.0105(5)	0.0081(4)	0	0.0057(3)	0	0.0096(2)
Si1	2	*e*	0.3080(1)	3/4	0.1891(1)	0.0056(5)	0.0113(7)	0.0098(5)	0	0.0035(4)	0	0.0087(3)
Si2	2	*e*	0.2074(1)	3/4	0.8040(1)	0.0052(5)	0.0104(6)	0.0087(5)	0	0.0034(4)	0	0.0078(3)
Si3	2	*e*	0.1630(1)	3/4	0.4982(1)	0.0081(5)	0.0074(6)	0.0069(5)	0	0.0040(4)	0	0.0071(3)
Mn1	2	*b*	1/2	0	1/2	0.0061(3)	0.0102(4)	0.0066(3)	0.0002(3)	0.0027(2)	−0.0002(3)	0.0075(2)
Mn2	2	*a*	1/2	0	0	0.0047(3)	0.0070(4)	0.0062(3)	0.0005(3)	0.0029(2)	0.0007(3)	0.0057(2)
Mn3	2	*c*	0	1/2	0	0.0048(3)	0.0087(4)	0.0078(3)	−0.0005(3)	0.0022(2)	−0.0007(3)	0.0071(2)
O1	4	*f*	0.2585(2)	0.5212(4)	0.4988(2)	0.0106(8)	0.009(1)	0.0106(9)	0.000(1)	0.0064(8)	−0.002(1)	0.0094(5)
O2	4	*f*	0.1937(2)	0.5340(5)	0.1622(2)	0.0087(8)	0.013(1)	0.0087(9)	0.001(1)	0.0010(7)	−0.001(1)	0.0106(5)
O3	4	*f*	0.3153(2)	0.5289(5)	0.8358(2)	0.0080(8)	0.012(1)	0.0080(9)	0.0020(9)	0.0011(7)	0.000(1)	0.0099(5)
O4	2	*e*	0.4213(4)	3/4	0.0929(4)	0.006(1)	0.033(2)	0.013(2)	0	0.004(1)	0	0.0174(9)
O5	2	*e*	0.4444(4)	3/4	0.3485(4)	0.007(1)	0.012(2)	0.014(2)	0	0.003(1)	0	0.0112(7)
O6	2	*e*	0.0866(2)	1/4	0.9348(3)	0.011(1)	0.008(2)	0.014(1)	0	0.007(1)	0	0.0101(7)
O7	2	*e*	0.4395(4)	1/4	0.3806(4)	0.006(1)	0.014(2)	0.015(2)	0	0.003(1)	0	0.0115(8)
O8	2	*e*	0.0726(4)	3/4	0.8761(4)	0.007(1)	0.015(2)	0.013(1)	0	0.006(1)	0	0.0106(7)
O9	2	*e*	0.0999(4)	3/4	0.6326(3)	0.008(1)	0.014(2)	0.009(1)	0	0.005(1)	0	0.0099(7)
O10	2	*e*	−0.0071(3)	3/4	0.3610(2)	0.012(1)	0.021(2)	0.003(1)	0	0.004(1)	0	0.0120(8)
O11	2	*e*	0.3983(3)	1/4	0.0631(2)	0.007(1)	0.025(2)	0.019(2)	0	0.006(1)	0	0.0168(8)
H6	2	*e*	0.2032(3)	1/4	0.978(4)							0.05
H10	2	*e*	−0.002(1)	3/4	0.2666(4)							0.05
H11	2	*e*	0.405(1)	1/4	0.1609(4)							0.05

* Multiplicity.
† Wyckoff letter.

TABLE 4. Selected interatomic distances (Å) and angles (°)

Mn1-O1 ×2	2.163(2)	Si1-O2 ×2	1.626(3)
Mn1-O5 ×2	2.098(3)	Si1-O4	1.644(4)
Mn1-O7 ×2	1.902(2)	Si1-O5	1.654(4)
mean	2.054	mean	1.638
Mn2-O3 ×2	1.902(2)	Si2-O3 ×2	1.619(3)
Mn2-O4 ×2	2.044(2)	Si2-O8	1.622(4)
Mn2-O11 ×2	1.992(2)	Si2-O9	1.673(3)
mean	1.979	mean	1.633
Mn3-O2 ×2	1.940(2)	Si3-O1 ×2	1.631(3)
Mn3-O6 ×2	1.927(2)	Si3-O9	1.661(4)
Mn3-O8 ×2	2.217(3)	Si3-O10	1.665(3)
mean	2.028	mean	1.647
Ca1-O1 ×2	2.423(3)	Ca2-O1 ×2	2.421(2)
Ca1-O2 ×2	2.383(3)	Ca2-O3 ×2	2.278(3)
Ca1-O7	2.290(3)	Ca2-O4	2.762(4)
Ca1-O8	2.326(3)	Ca2-O5	2.460(4)
Ca1-O9	2.637(3)	Ca2-O10	2.459(3)
mean	2.409	mean	2.440
O10···O6	2.849(4)	O11···O2	2.945(3)
O10-H10···O6	156.2(5)	O11···O7	3.133(4)
O6···O11	2.631(2)	O11-H11···O2	103.2(3)
O6-H6···O11	175.5(10)	O11-H11···O7	175.4(6)
O2-Si1-O2	107.5(2)	O3-Si2-O3	112.0(2)
O2-Si1-O4 ×2	112.6(1)	O3-Si2-O8 ×2	113.4(1)
O2-Si1-O5 ×2	115.6(1)	O3-Si2-O9 ×2	107.0(1)
O4-Si1-O5	101.0(2)	O8-Si2-O9	103.3(2)
O1-Si3-O1	116.9(2)		
O1-Si3-O9 ×2	109.2(1)		
O1-Si3-O10 ×2	109.01(9)		
O9-Si3-O10	102.6(2)		

TABLE 5. Refined site-scattering values* and assigned site populations† for the Mn1, Mn2, Mn3, Ca1, and Ca2 sites

Site	Site-scattering	Site population (apfu)	Number of electrons‡
Mn1	23.26(6)	0.82Mn + 0.06Al + 0.09Mg + 0.03Cu	23.23
Mn2	21.98(6)	0.75Mn + 0.25Al	22.00
Mn3	24.34(6)	0.95Mn + 0.05Al	24.40
Ca1	19.87(7)	1.00Ca	20.00
Ca2	19.94(7)	1.00Ca	20.00

* The site-scattering values were determined from the site occupancies of calcium at Ca1 and Ca2 and manganese at Mn1, Mn2, and Mn3, refined without any constraints.

† Elements less than 0.1 wt% by EPMA analysis were neglected.

‡ Calculated from the site populations.

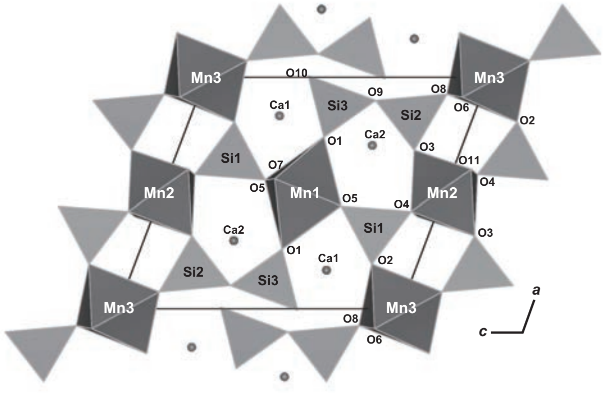

FIGURE 3. Crystal structure of macfallite projected down [010] using the program VESTA (Momma and Izumi 2006).

(2) divalent cations such as Mg^{2+} and Cu^{2+} were assigned to the Mn1 site, because the volume of the $Mn1O_6$ octahedron is the largest among three independent MO_6 octahedra; and (3) the following constraints were applied: g (Mn) + g (Al) = 1 for the Mn2 and Mn3 sites and g (Mn) + g (Al) = 1 – g (Mg) – g (Cu) for the Mn1 site, where g represents site population (apfu). The resulting cation populations are 0.82 Mn + 0.06 Al + 0.09 Mg + 0.03 Cu for Mn1, 0.75 Mn + 0.25 Al for Mn2 and 0.95 Mn + 0.05 Al for Mn3 (Table 5).

Bond-valence sums were calculated using the electrostatic strength function of Brown and Altermatt (1985) and the bond-valence parameters of Brese and O'Keeffe (1991). The results are given in Table 6. Both bond-valence sums and the determined hydrogen positions indicate that hydroxyl groups are located at the O6, O10, and O11 positions. Although the O10 position, which was labeled as O5 in Moore et al. (1985), was considered by them to be occupied only by oxygen, the bond-valence sum for this position indicates that a hydroxyl group can also be located here. In addition, contrary to the proposal that the O7 position consists of an OH group (Moore et al. 1985), both oxygen atoms and OH groups can be assigned to this site (see below).

DISCUSSION

Cation distributions at the octahedral sites

Moore et al. (1985) determined site occupancies for the Mn2 site in macfallite as 0.61(2) Mn^{3+} + 0.39 Al^{3+}, whereas the Mn1 and Mn3 sites were assumed to be completely filled with Mn^{3+}. The presence of Al at the Mn2 site is confirmed by the results obtained in this study giving 0.75 Mn + 0.25 Al. However, our results indicate that a small amount of Al may also be assigned to Mn1 and Mn3 with 0.06 and 0.05 apfu Al, respectively. In addition, our microprobe results indicate that small concentrations of Mg^{2+} (0.09 apfu) and Cu^{2+} (0.03 apfu) can also occur in macfallite. Divalent cations are assigned to Mn1, because of the nature of the polyhedral volumes, whereby the MO_6 octahedral volumes decrease in the order Mn1 > Mn3 > Mn2.

Crystal chemical relationships between macfallite, sursassite, and pumpellyite

The crystal structures of macfallite, sursassite of formula $Mn^{2+}Al_3Si_3O_{11}(OH)_3$ and pumpellyite ($Z = 1$, space group $A2/m$) of formula $Ca_8X^{VI}_4Y^{VI}_8Si_{12}O_{56-n}(OH)_n$, are closely related to each other (Allmann 1984; Mellini et al. 1984; Moore et al. 1985; Ferarris et al. 1986). Moore et al. (1985) analyzed the crystal chemistry of the group of so-called 6 × 9 Å sheet structures, namely lawsonite, sursassite, macfallite, and pumpellyite. All their structures contain a ${}^{2}_{\infty}[M^{3+}_{2}\square\phi_{2}(TO_{4})_{2}]_{2}$-sheet. In projections along their 6 Å axes (i.e., the b axis in macfallite), these structures show two different infinite chains consisting of edge-sharing MO_6 octahedra (labeled M2 and M3 in macfallite and sursassite and Y in pumpellyite). They are linked to one another along the 9 Å axis (i.e., a axis in macfallite) by TO_4 tetrahedra (i.e., Si1 and Si2 in macfallite). The vacancy symbol □ in the structural unit represents a third "empty structural column" running parallel to the former two chains of octahedra (Fig. 4). It is represented in projections onto (010) as narrow channels having a rhomboidal cross section.

TABLE 6. Calculated bond valences (v.u.) in macfallite

Cation/ anion	Ca1	Ca2	Mn1	Mn2	Mn3	Si1	Si2	Si3	ΣC^v	Anion chemistry
O1	0.277†	0.278†	0.323†					1.025†	1.903	O^{2-}
O2	0.305†				0.606†	1.039†			1.950	O^{2-}
O3		0.394†		0.632†			1.058†		2.084	O^{2-}
O4		0.121		0.432†,‡		0.989			1.974	O^{2-}
O5		0.253	0.385‡,†			0.963			1.986	O^{2-}
O6					0.627‡,†				1.254	OH^-
O7	0.383‡		0.654†						1.691	O^{2-}
O8	0.350				0.287‡,†		1.050		1.974	O^{2-}
O9	0.164						0.915	0.945	2.024	O^{2-}
O10		0.253						0.935	1.188	OH^-
O11				0.496†					0.992	OH^-
ΣA^v	2.061	1.989	2.724	3.120	3.040	4.030	4.081	3.930		

Notes: ΣA^v is the valence of bonds emanating from cation summed over the bonded anions. ΣC^v is the valence of bonds reaching anions.
† Two bonds per cation.
‡ Two bonds per anion.

Divalent cations are located at the Mn1 site in macfallite and at the *X* site in pumpellyite. The volume of the $Mn1O_6$ octahedron (11.3 Å^3) in macfallite is similar to that of the XO_6 octahedron in pumpellyite (10.3–12.0 Å^3: Galli and Alberti 1969; Allmann and Donnay 1973; Yoshiasa and Matsumoto 1985; Artioli and Geiger 1994; Artioli et al. 2003; Brigatti et al. 2006; Nagashima et al. 2006; Hatert et al. 2007; Nagashima and Akasaka 2007). In the case of sursassite, previous studies (e.g., Heinrich 1962; Allmann 1984; Mellini et al. 1984; Reinecke 1986; Minakawa and Momoi 1987) implied that small amounts of divalent cations, such as Mg, are distributed over the octahedral sites, although the possibility of intergrowths with pumpellyite (Mellini et al. 1984) has also to be considered. The preferred site for Mg in sursassite is Al1 because it has the largest volume (10.7 Å^3: Allmann 1984; 10.3 Å^3: Mellini et al. 1984) among its three octahedral sites. On the basis of structural topology, M1 in macfallite (i.e., Mn1) and sursassite (Al1) are most closely related to the *X* site in pumpellyite, whereas M2 and M3 in macfallite (i.e., Mn2 and Mn3) and sursassite (Al2 and Al3) are related to the Y site in pumpellyite. This assignment is also supported by the cation distribution over the octahedral sites and the size of the MO_6 octahedra.

It should be noted, however, that the angular distortion for the $Mn1O_6$ octahedron in macfallite is greater than that for the $Mn2O_6$ and $Mn3O_6$ octahedra (Table 7), which is opposite to the angular distortion found for corresponding octahedra in pumpellyite and sursassite. In addition, the degree of octahedral bond length distortion in macfallite is more pronounced than that in sursassite (Allmann 1984; Mellini et al. 1984). The reason may be related to a Jahn-Teller effect arising from the presence of Mn^{3+} in macfallite.

Hydrogen bond systems in macfallite and sursassite

The positions of the hydrogen atoms and directions of the hydrogen bonds in macfallite are shown in Figure 4. All O-H bonds are located in mirror planes that are parallel to (010). This is also the situation in pumpellyite (Yoshiasa and Matsumoto 1985; Brigatti et al. 2006; Nagashima and Akasaka 2007). The relationships between donor and acceptor O atoms and their hydrogen-bonding in macfallite can be summarized as follows: O10-H10···O6, O6-H6···O11, O11-H11···O2, and O11-H11···O7. The O10H10 hydroxyl group terminates the disilicate unit and represents a so-called silanol group. O6 acts as an acceptor of this weak hydrogen bond (Fig. 4). Following this, the general structural formula of macfallite can be presented as $Ca_2(Mn^{3+}, Al)_3(OH)_2[SiO_4][Si_2O_6(OH)]$.

The IR spectrum in the region of the OH-stretching vibrations is characterized by three OH bands at 3413, 3376, and 3239 cm^{-1}, and one broad band at 2900 cm^{-1}. The associated OH···O distances (Table 8) were calculated using the correlation between the observed OH-band wave number and the O···O separation in Å as given by Libowitzky (1999). The three strongest OH bands result from relatively weak hydrogen bonds associated with the O10 and O11 sites, in agreement with the H positions determined by X-ray and the bond valence sum analysis. The broad band at ca. 2900 cm^{-1} is assigned to an OH stretch associated with the O6-H6···O11 bond with an O···O separation of about 2.63 Å. In macfallite, O6 and O11 (ϕ-type sites) occur on the channel walls and they contain OH groups that compete to form a hydrogen bond toward the diagonally adjacent ϕ site. The resulting hydrogen bonding occurs inside the narrow channels, and it gives rise to the band at ca. 2900 cm^{-1}. The O6 and O11 site are associated with bond-valence values of 1.25 and 0.99 valence units (v.u.), respectively. This is due to development of Mn^{3+} Jahn-Teller distortion in the columns formed by Mn2 and Mn1 octahedra. Because the bond-valence value for O11 is less than that of O6 (Table 6), O11 can act as both a donor and an acceptor for a stronger hydrogen bond, whereas O6 acts as a donor and acceptor for a weaker hydrogen bond. Ferraris and Ivaldi (1988) showed that for short O-H···O donor-acceptor distances, the acceptor benefits from an additional ca. 0.25 v.u. Thus, O11, with the smaller bond-valence value, acts as an acceptor from O6-H6 to form a relatively strong hydrogen bond. The O11-H11 group has to adjust to this hydrogen bonding arrangement. This gives rise to a bifurcated hydrogen bond, where H11 is bonded to both O2 and O7. Similar broad IR bands at low wave number are

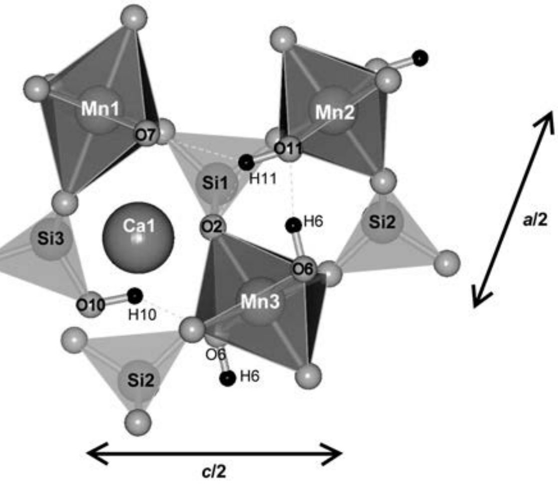

FIGURE 4. Hydrogen positions and hydrogen bonds in macfallite projected down [010]. Dashed lines indicate H···O bonds.

TABLE 7. Angular and bond length distortions for the octahedral sites of macfallite and structurally related minerals

Mineral	Mn1 site			Mn2 site			Mn3 site			Reference
	$\sigma_\theta(\mathrm{oct})^2$	$<\lambda_{\mathrm{oct}}>$	*DI*	$\sigma_\theta(\mathrm{oct})^2$	$<\lambda_{\mathrm{oct}}>$	*DI*	$\sigma_\theta(\mathrm{oct})^2$	$<\lambda_{\mathrm{oct}}>$	*DI*	
Macfallite	33.60	1.016	0.049	24.65	1.009	0.026	19.13	1.014	0.062	This study
Macfallite	31.58	1.015	0.049	26.39	1.010	0.026	18.04	1.013	0.060	Moore et al. (1985)
	Al1 site			Al2 site			Al3 site			
Sursassite	14.16	1.007	0.033	37.08	1.011	0.008	26.31	1.010	0.030	Allmann (1984)
Sursassite	19.94	1.009	0.033	30.51	1.009	0.006	27.85	1.010	0.026	Mellini et al. (1984)
Pumpellyite group	*X* site			*Y* site						
HR	21.08	1.008	0.030	31.63	1.011	0.026				Galli and Alberti (1969)
Julgoldite	14.55	1.006	0.029	29.59	1.009	0.014				Allmann and Donnay (1973)
Pumpellyite	16.83	1.007	0.028	37.46	1.012	0.022				Yoshiasa and Matsumoto (1985)
HR	18.20	1.006	0.011	28.39	1.009	0.018				Artioli and Geiger (1994)
K1	26.64	1.010	0.030	34.01	1.010	0.022				"
BU	19.79	1.008	0.027	30.16	1.009	0.019				"
Julgoldite-(Fe^{3+})	5.98	1.002	0.018	16.30	1.005	0.012				Artioli et al. (2003)
MTS	14.41	1.007	0.034	36.39	1.012	0.021				Nagashima et al. (2006)
KGH	18.41	1.008	0.035	35.25	1.011	0.022				"
Poppiite	18.74	1.007	0.027	29.40	1.009	0.019				Brigatti et al. (2006)
Pumpellyite-(Al)	12.07	1.004	0.020	29.69	1.011	0.029				Hatert et al. (2007)
Chromian pumpellyite	13.56	1.005	0.019	37.69	1.012	0.021				Nagashima and Akasaka (2007)

Note: HR, K1, and BU are sample labels given by Galli and Alberti (1969) and Artioli and Geiger (1994). $<\lambda_{\mathrm{oct}}> = \sum_{i=1}^{6}(l_i - l_0)^2/6$ (l_i = each bond length, l_0 = center-to-vertex distance for an octahedron with O_h symmetry, whose volume is equal to that of a distorted octahedron with bond lengths l_i) (Robinson et al. 1971), *DI*(oct) $= 1/6\Sigma|R_i - R_{\mathrm{avg}}|/R_{\mathrm{avg}}$ (R_i = each bond length; R_{avg} = average distance for an octahedron) (Baur 1974), and $\sigma_\theta(\mathrm{oct})^2 = \sum_{i=1}^{12}(\theta_i - 90^\circ)^2/11$ (θ_i = O–*M*–O angle) (Robinson et al. 1971).

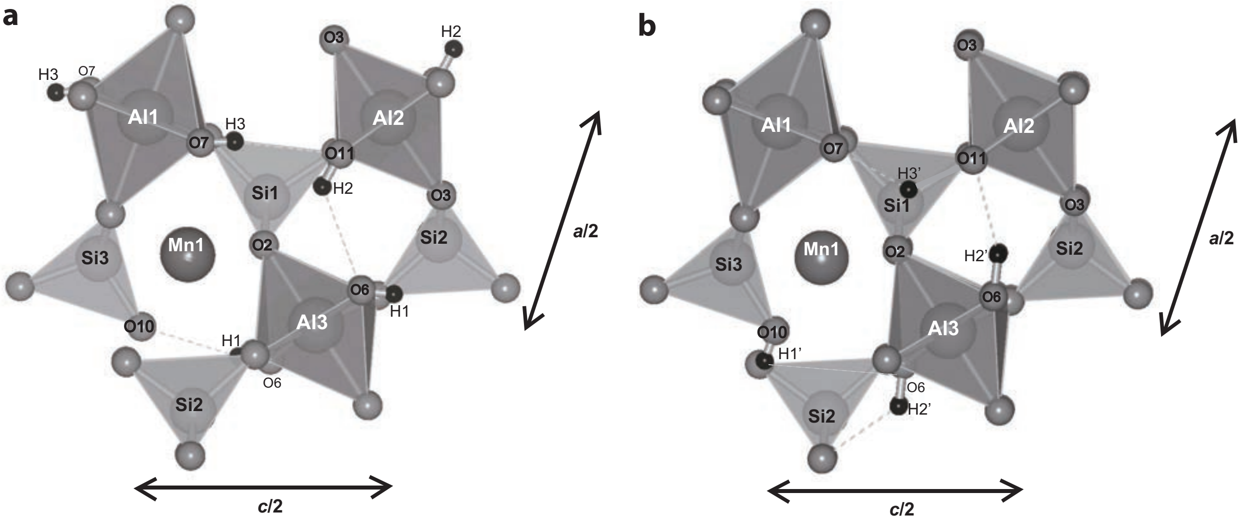

FIGURE 5. Hydrogen-bond system in sursassite proposed by Mellini et al. (1984); (**a**) with H1, H2, and H3 positions; (**b**) with H1′, H2′, and H3′ positions.

TABLE 8. Hydroxyl streching wave number and corresponding O···O distance in macfallite, as determined using the correlation from Libowitzky (1999)

OH stretching wave number (cm^{-1})	*d* (O···O) (Å)
3413	2.81
3376	2.78
3239	2.72
2900	2.63

also observed in sursassite (Reddy and Frost 2007), pumpellyite (Hatert et al. 2007), and lawsonite (Libowitzky and Rossman 1996). The origin of their OH bands is similar. These minerals also have relatively strong hydrogen bonds that cross narrow channels in their crystal structures.

Because of Mn^{3+} Jahn-Teller distortion, isostructural mozartite $CaMn^{3+}SiO_4(OH)$ and vuagnatite $CaAlSiO_4(OH)$ show a different arrangement of hydrogen-bond acceptors and donors (Nyfeler et al. 1997). Thus, it is not clear whether isostructural macfallite (M: Mn^{3+}) and sursassite (M: Al) have an identical system of hydrogen bonds. Mellini et al. (1984) suggested that in sursassite two different hydrogen-bond systems are present in equal proportions namely: O7-H3···O11-H2···O6-H1···$O10^{II}$ (Fig. 5a) and O7···H3′-O11···H2′-O6···H1′-$O10^{II}$ (Fig. 5b). In this model, the O6 and O11 sites always contain hydroxyl groups, whereas O7 and O10 can be occupied by either hydroxyl or oxygen anions on a local scale. In our reinterpretation of the hydrogen-bond system in sursassite, we propose that the occurrence of a specific set of hydrogen bonds depends on the degree of M^{2+} substitution at Al1. With only M^{3+} cations on Al1 there are only three hydrogen bonds labeled as H1′, H2′, and H3′ (Mellini et al. 1984) corresponding to the situation in macfallite. With some M^{2+} substitution at Al1 in sursassite, there will be an additional OH group at O7 coordinating Al1. Bond-valence calculations for sursassite, based on the structural data of Allmann (1984) and Mellini et al. (1984), suggest that Mg occurs preferentially at Al1. This requires, for charge balance reasons, an OH group at O7, with O11 acting as the acceptor of the hydrogen bond. Therefore, the OH group at O11 cannot form a hydrogen bond to O7 as an acceptor (Fig. 5b), but instead must reorient toward the center of the narrow structural channels with O6 as an acceptor (Fig. 5a). Subsequently, the hydrogen bond associated with O6 as a donor must also be different from the corresponding one in macfallite. Mellini et al. (1984) suggest that O6-H1 develops a strong hydrogen bond to O10, the terminal anion of the Si_2O_7 unit. Finally, O10 also represents an OH group and with O6 probably acting as an acceptor. However, the exact orientation of this bond is uncertain, because the H position of Mellini et al. (1984) is located only 1.58 Å from Mn2, which is very short indeed. Thus, a restudy of the hydrogen-bond system in sursassite is mandatory.

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