

Holtstamite, $\text{Ca}_3(\text{Al}, \text{Mn}^{3+})_2(\text{SiO}_4)_{3-x}(\text{H}_4\text{O}_4)_x$, a new tetragonal hydrogarnet from Wessels Mine, South Africa

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Abstract: A new tetragonal hydrogarnet from Wessels Mine, South Africa is described. The mineral occurs in a calc-silicate skarn together with Mn-rich vesuvianite, calcite and henritermierite. It is the Al-dominant analogue of henritermierite, $\text{Ca}_3\text{Mn}_2(\text{SiO}_4)_2(\text{OH})_4$, space group $I4_1/acd$. The new mineral, holtstamite, is optically uniaxial positive and shows lower refractive indices, $\omega = 1.718$ (2) and $\varepsilon = 1.746$ (2), than henritermierite. The cell parameters of holtstamite are $a = 12.337$ (3) and $c = 11.930$ (5) Å.

Extensive holtstamite-henritermierite solid solution is evident from compositionally zoned grains, which frequently show cores of henritermierite composition and rims of holtstamite. The octahedral occupancy in holtstamite is characterised by $\text{Al} > \text{Mn}^{3+}$ and the most Al-rich tetragonal hydrogarnets in the present sample contain 69 mol.% of a hypothetical tetragonal end-member $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_2(\text{OH})_4$.

A crystal structure refinement ($R1 = 3.57$ %) of a zoned holtstamite single crystal with the mean composition $\text{Ca}_3(\text{Al}_{0.96}\text{Mn}_{0.68}\text{Fe}_{0.37})(\text{SiO}_4)_{2.00}(\text{H}_4\text{O}_4)_{0.99}$ shows distinctly shorter octahedral bond lengths (mean M1-O = 1.976 Å) than for henritermierite (mean M1-O = 2.020 Å) and a considerably smaller octahedral axial ratio (1.085) as compared to henritermierite (1.144).

Crystal field splitting parameters, $10Dq$, for Mn^{3+} in crystals on the join henritermierite-holtstamite indicate strong structural relaxation, which is the most likely cause for the observed complex FTIR-spectrum of holtstamite in the OH-stretching region.

It is suggested that stabilisation of the tetragonal Al-dominant calcic hydrogarnet may require a fraction of Mn^{3+} at the octahedral M1-site. Micro-chemical analyses indicate that Si and OH are inversely correlated in holtstamite, with higher degree of H_4O_4 -substitution for SiO_4 in Al-rich compositions. Due to variable OH-content as well as a necessary stabilisation by the presence of trivalent manganese, the holtstamite formula is defined as $\text{Ca}_3(\text{Al}, \text{Mn}^{3+})_2(\text{SiO}_4)_{3-x}(\text{H}_4\text{O}_4)_x$ (with $\text{Al} > \text{Mn}^{3+}$) rather than $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_2(\text{OH})_4$. In the present crystals $0.9 < x < 1.2$, but the limits of H_4O_4 - SiO_4 substitution as well as maximum Al-occupancy at the octahedral site need to be explored.

Key-words: new mineral, crystal structure, hydrogarnet, holtstamite, South Africa.

Introduction

A number of different cubic hydrogarnets are encountered in various geological settings, of which the most widespread are the hydrogrossular species hibschite and katoite (*e.g.*, Ferro *et al.*, 2003; Passaglia & Rinaldi, 1984), $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$, with $x < 2$ and $x > 2$, respectively. Additional cubic hydrogarnets comprise Fe-rich andraditic species (*e.g.*, Armbruster, 1995). The only tetragonal hydrogarnet observed so far in nature is henritermierite, $\text{Ca}_3\text{Mn}_2(\text{SiO}_4)_2(\text{OH})_4$, which has been described from Morocco (Gaudefroy *et al.*, 1969 and Aubry *et al.*, 1969) and South Africa (Cairncross *et al.*, 1997 and Armbruster *et al.*, 2001). In the course of a study on vesuvianite, small amounts of strongly zoned grains of an Al-rich tetragonal hydrogarnet were encountered in a small sample of vesuvianite-rich skarn from Wessels Mine, South Africa. Micro-

chemical analyses showed some of the grains to contain zones of Al-dominant compositions. In the present paper we present a description, including a crystal structure refinement and spectroscopic data, of this new tetragonal hydrogarnet.

The mineral is named after Dr. Dan Holtstam (b. 1963) honouring his contributions to the mineralogy of Mn-deposits of Långban type. The Commission on New Mineral and Mineral Names of the International Mineralogical Association (IMA) has approved the mineral and mineral name.

Samples

The new tetragonal hydrogarnet, holtstamite, occurs in vesuvianite-rich skarns formed by hydrothermal alteration of primary sedimentary manganese ores at Wessels Mine, Ka-

lahari manganese field, South Africa. Associated minerals comprise Mn^{3+} -bearing vesuvianite, calcite and henritermierite. Grains (up to 3 mm), of holtstamite are scarce in the cm-sized vesuvianite specimen that contains the new mineral. These few rounded grains of holtstamite are composed of small (<0.4 mm) commonly twinned crystals, which invariably show colour zoning. Occasionally, the crystals make up pseudo-octahedra indicating twinning around [111]. The crystal cores are normally darker in colour than the rims, which was demonstrated by micro-chemical analyses to be due to chemical zoning with relatively higher Al-contents in crystal rims and higher Mn- and/or Fe-concentrations in crystal cores. The zoning is rarely a simple core-rim variation but rather oscillatory.

Holtstamite is transparent and has a vitreous lustre. The colour of the mineral is pale brownish yellow and in thin section it shows a weak pleochroism with O = pale orange yellow and E = lemon yellow. Absorption is $E > O$. The mineral is uniaxial positive (+) with $\omega = 1.718$ (2) and $\epsilon = 1.746$ (2) (white light on crystal WOS of Table 2). These values are considerably lower than those, $\omega = 1.7982$ and $\epsilon = 1.78747$, recorded ($\lambda = 577$ nm) for henritermierite (Armbruster *et al.*, 2001). Mohs' hardness of holtstamite is ≈ 6 and the mineral is brittle and shows conchoidal fracturing without any distinct cleavage directions. The calculated density, using refined cell parameters and the composition of the most Al-rich crystal, equals 3.25 g/cm^3 . Type material is deposited in the mineral collections of the Swedish Museum of Natural History, Stockholm.

For reference purposes, electron microprobe analyses and FTIR- and optical absorption spectra of single crystals from a monomineralic henritermierite sample from the N'Chwaning mine, South Africa, were recorded.

Experimental techniques

Concentrations of heavier elements ($Z \geq 9$) were determined by electron microprobe techniques, using a Cameca SX50 instrument operated at 20 kV accelerating potential and 12 nA sample current. Standard samples comprised albite (Na and Si), Al_2O_3 (Al), MgO (Mg), MnTiO_3 (Mn, Ti), Fe_2O_3 (Fe) and wollastonite (Ca). Wavelength dispersive scans revealed no detectable amounts of any additional elements. Raw data were reduced by means of the PAP-routine (Pouchou & Pichoir, 1991). Mineral formulae were calculated in accordance with henritermierite on the basis of 24 negative charges and H_2O -contents were calculated assuming that $[\text{SiO}_4] + [\text{H}_4\text{O}_4]$ equals three.

Due to scarcity of material as well as the chemical zoning of the crystals it was not possible to obtain direct high-resolution water analyses on holtstamite. In order to explore the presence and character of H-species in holtstamite, an unpolarised FTIR-spectrum of a single crystal, which was ground and double-sided polished on (001), was acquired. The recorded spectrum consequently corresponds to an O-spectrum. For comparison, an unpolarised spectrum on a (001)-platelet of henritermierite from the N'Chwaning mine, South Africa, was also recorded. FTIR-spectra were acquired during 128 cycles at a spectral resolution of 4 cm^{-1}

with a Bruker Equinox 55S FTIR-microscope-spectrometer equipped with a glowbar source, KBr beamsplitter and a MCT-detector.

In order to determine the manganese valence state, polarised single-crystal electronic spectra of holtstamite, and for reference of henritermierite, were acquired with a Zeiss MPM 800 single beam microscope spectrometer using a 75 W Xenon arc lamp and a 100 W tungsten lamp as light source in the UV-VIS region (350–800 nm) and the NIR region (800–2000 nm), respectively. A photomultiplier and a photoconductive PbS-cell served as detectors in the two respective spectral regions. Concave holographic gratings were used as monochromators and a UV-transparent Glan-Thompson prism served as polariser. For the UV-VIS range, the spectral resolution was set at 1 nm and spectra were recorded at 1 nm steps during three cycles, while resolution and step size were both 5 nm in the NIR-region. The diameter of the measuring spot was 40 μm . The crystal area measured for optical absorption was subsequently carbon coated and analysed by means of electron microprobe techniques. Orientation of the measured crystals was aided by crystal morphology and optical examination under the polarising microscope using conoscopic illumination. The oriented crystals were embedded in a thermoplastic resin with retained orientation. After resin hardening, the absorbers were ground and polished on two parallel surfaces producing slabs of single-crystal absorbers. The final thickness of the double-sided polished single crystals was determined by means of a digital micrometer.

X-ray powder diffraction data were recorded with a Philips PW1710 diffractometer using graphite-monochromatised $\text{CuK}\alpha$ -radiation on a tiny powder sample mounted on a Si-plate. The mineral powder was prepared from a small number of selected pale-coloured (assumably Al-rich) holtstamite crystals. The recorded powder pattern was indexed according to tetragonal henritermierite and lattice parameters obtained from a least-square refinement (Novak & Col-

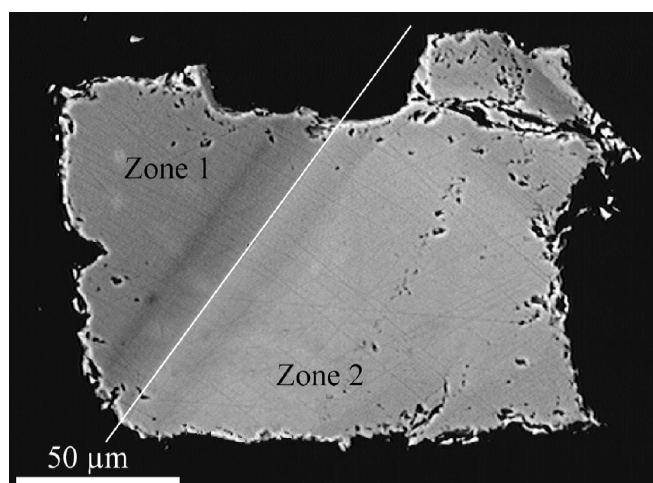


Fig. 1. BSE micrograph of holtstamite crystal WX1, which was used for refinement of the mineral structure. The darker Al-rich "zone 1" (analysis WX1A of Table 1) constitutes ca. 35 % of the crystal surface, while the brighter Al-poorer and Fe-richer "zone 2" (analysis WX1B) dominates the crystal. The white solid line delineates the border between the two compositionally distinct zones.

Table 1. Details of single-crystal X-ray diffraction and refinement of holtstamite.

Crystal size (μm)	170x130x90
T (K)	293(2)
Reflections measured	7704
Unique reflections	549
Max θ	28.02
Space group	$I4_1/acd$ (No. 142)
Cell dimensions (\AA)	$a = 12.337(3)$ $c = 11.930(5)$
$R(\text{int})$	6.42 %
$R(\sigma)$	2.68 %
$\mu\Delta(\text{mm}^{-1})$	3.58
$R1, F_o > 4\sigma(F_o)$	3.57 %
Number of l.s. parameters	58
GooF	1.169
$wR2$	9.17 %

Lattice parameters were obtained from diffractometer powder pattern; Cu K α , 23 °C

$$R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$wR2 = \frac{[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}}{\sum [w(F_o^2)^2]^{0.5}}$$

$$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP] \text{ and } P = [2F_c^2 + \text{Max}(F_o^2, 0)]/3$$

$$\text{GooF} = \frac{[\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{0.5}}{\sum [w(F_o^2)^2]^{0.5}}$$

ville, 1989) of 46 measured and indexed lines. The following data were obtained: $a = 12.337(3)$ Å, $c = 11.930(5)$ Å. Due to extensive twinning and chemical zoning it was difficult to find a crystal suitable for single crystal structural refinement. The crystal finally selected shows no twinning and a comparatively simple chemical zoning pattern (Fig. 1). Intensity data for this single crystal was collected at room temperature on a STOE IPDS diffractometer (Stoe & Cie, 1996a) with monochromatic MoK α radiation ($\lambda = 0.71073$ Å). Inspection of several reciprocal layers perpendicular to c^* revealed that reflections were rather broad and partly elongated along a^* , which we attribute to chemical zoning in the selected crystal. The quality of the data, however, was satisfactory as manifested by the internal R-value and the refinement residuals (Table 1). The data set was corrected for Lorentz and polarisation effects. A numerical absorption correction was performed by the program X-SHAPE (Stoe & Cie, 1996b). The centrosymmetric space group $I4_1/acd$ was assigned on the basis of the systematic absences and the statistical analysis of the intensity distributions. Structure refinement (full-matrix least-squares on F^2) was performed with the program SHELX-97 (Sheldrick, 1997) using the atomic position parameters of henritermierite as starting values. The M1-position (site 16c) was refined as mixed occupied by Mn and Al. The H-position was introduced corresponding to henritermierite (O3-H) and could be refined isotropically. In analogy to henritermierite (Armbruster *et al.*, 2001), a weak electron density peak in the difference Fourier map at the Si2-position (site 8a at the centre of O3 tetrahedron) was observed and refined as Si with variable occupancy. In the refinement of henritermite (Armbruster *et al.*, 2001), the O3-position was split (O3, O3A) in order to create more reasonable Si-O distances for the weakly occupied H_4O_3 tetrahedron centre. From our holtstamite data, however, there was no indication that could justify the introduction of such a split. Further, con-

trary to henritermierite, we detected a partial site occupancy (8 % deficiency) of the Si1-site (16e) in holtstamite. The final residual electron density was $\pm 0.5 \text{ e/\AA}^3$, the refinement residuals can be considered as satisfactory. Details of the single-crystal data collection and refinement are listed in Table 1.

Results and discussion

The composition of tetragonal hydrogarnets in the present specimen range from *ca.* 23 to *ca.* 69 mol. % of a hypothetical $\text{Ca}_3(\text{Al}^{3+})_2(\text{SiO}_4)_2(\text{OH})_4$ -molecule. The majority of the analysed crystals in the present specimen show octahedral site compositions from $\sim(\text{Al}_{0.60}\text{Mn}_{0.35}\text{Fe}_{0.05})_2$ to $\sim(\text{Al}_{0.50}\text{Mn}_{0.45}\text{Fe}_{0.05})_2$, *i.e.* they are Al-dominant (Fig. 2). Most crystals show compositional zoning with Mn and/or Fe-richer cores and rims containing ca 65 % of the hypothetical $\text{Ca}_3(\text{Al}^{3+})_2(\text{SiO}_4)_2(\text{OH})_4$ -molecule. The crystal used for structural refinement displays a simple zoning pattern (Fig. 1 and Table 2) and a mean composition of $\text{Ca}_3(\text{Al}_{0.96}\text{Mn}^{3+}_{0.68}\text{Fe}^{3+}_{0.37})(\text{SiO}_4)_{2.00}(\text{H}_4\text{O}_4)_{0.99}$.

Results of the single-crystal refinement of holtstamite crystal WX1, including atomic position parameters and selected interatomic distances are summarised and compared with corresponding data for henritermierite (Armbruster *et al.*, 2001) in Tables 3 and 4, respectively. The tetragonal structure of holtstamite ($Z = 8$) is, in analogy with henritermierite, conveniently displayed as a polyhedral framework consisting of M1O_6 octahedra and SiO_4 tetrahedra connected by sharing corners (Fig. 3). This framework exhibits channels along [001] in which one type of Ca atoms (Ca2) is situated. The unit cell volume of henritermierite is slightly larger than that of holtstamite, which is mainly due to the considerably reduced a lattice parameter in the latter.

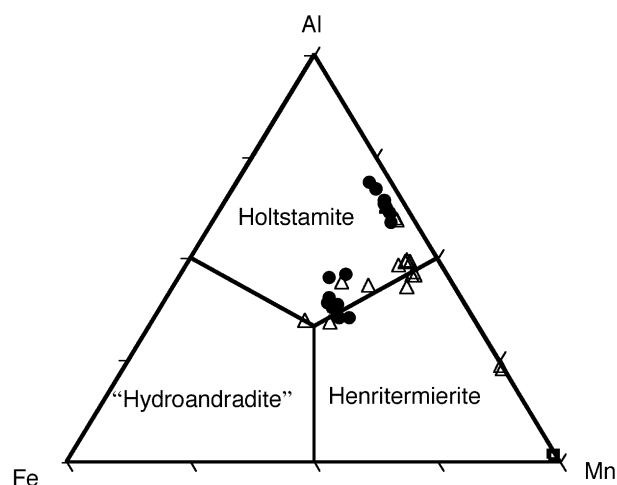


Fig. 2. Triangular diagram (Al-Mn-Fe) summarising individual analyses of the present tetragonal hydrogarnets. Filled circles represent analytical data obtained on the crystal used for structure refinement (WX1), open triangles show analyses from additional hydrogarnet crystals in the present Wessels sample and open squares (at the Mn-corner) symbolise compositions of the N'Chwaning henritermierite (analysis NIROS of Table 1).

Table 2. Microprobe analyses of holtstamite and henritermierite.

	Holtstamite Wessels Mine										Henritermierite N'Chwaning				
	WX1A N=6		WX1B N=9		Crystal mean	WIR N=4		WOS N=4		W1 N=3		W2 N=9		NIROS N=9	
	Mean	s.d.	Mean	s.d.		Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
SiO ₂ (wt. %)	24.91	0.51	26.99	0.37	26.26	24.28	0.16	24.60	0.30	25.74	0.21	25.58	0.31	25.03	0.36
Al ₂ O ₃	14.68	1.07	8.67	0.97	10.77	13.79	0.34	14.67	0.67	4.93	0.08	10.41	0.48	0.42	0.06
Mn ₂ O ₃	11.36	1.11	11.80	0.77	11.64	12.16	0.59	11.26	0.54	24.93	0.35	15.35	0.56	32.00	0.34
Fe ₂ O ₃	1.56	0.17	8.86	0.69	6.30	1.29	0.06	1.41	0.07	0.13	0.00	2.70	0.43	0.24	0.07
CaO	37.80	0.21	36.20	0.19	36.76	37.76	0.27	37.87	0.05	35.46	0.16	37.11	0.29	34.24	0.16
H ₂ O _{calc}	9.39	0.53	7.05	0.37	7.87	9.48	0.24	9.52	0.28	7.15	0.01	8.27	0.30	7.25	0.23
SUM	99.69	0.36	99.56	0.39	99.61	98.78	0.67	99.33	0.41	98.33	0.64	99.42	0.76	99.17	0.57
Atoms per formula unit based on 24 negative charges and (SiO ₄ +[H ₄ O ₄]) = 3															
Si	1.846	0.054	2.090	0.041	2.004	1.817	0.021	1.823	0.033	2.050	0.00s	1.949	0.029	2.023	0.032
Al	1.282	0.081	0.791	0.081	0.963	1.216	0.033	1.281	0.050	0.463	0.00	0.935	0.040	0.040	0.005
Mn	0.641	0.068	0.695	0.050	0.676	0.693	0.031	0.636	0.036	1.511	0.02	0.890	0.032	1.968	0.013
Fe	0.087	0.00	0.516	0.043	0.366	0.073	0.004	0.079	0.003	0.008	0.000	0.154	0.025	0.015	0.005
Ca	3.001	0.023	3.003	0.018	3.002	3.027	0.012	3.007	0.022	3.026	0.003	3.030	0.03	2.965	0.014
H/4 _{calc}	1.147	0.054	0.907	0.041	0.991	1.184	0.023	1.177	0.032	0.950	0.005	1.052	0.032	0.977	0.029
End-member ¹ fractions (mol. %)															
Holtstamite	63.8	3.7	39.5	3.8	48.0	61.4	1.6	64.2	1.9	23.4	0.5	47.2	1.9	2.0	0.3
Henritermierite	31.9	3.5	34.7	2.6	33.7	35.0	1.8	31.9	2.0	76.3	0.5	45.0	1.6	97.3	0.3
„Hydroandradite“	4.3	0.5	25.8	2.2	18.3	3.7	0.2	3.9	0.2	0.4	0.0	7.8	1.3	0.7	0.2

¹End-member fractions were calculated under the assumption of pure Al, Mn, and Fe end member compositions.

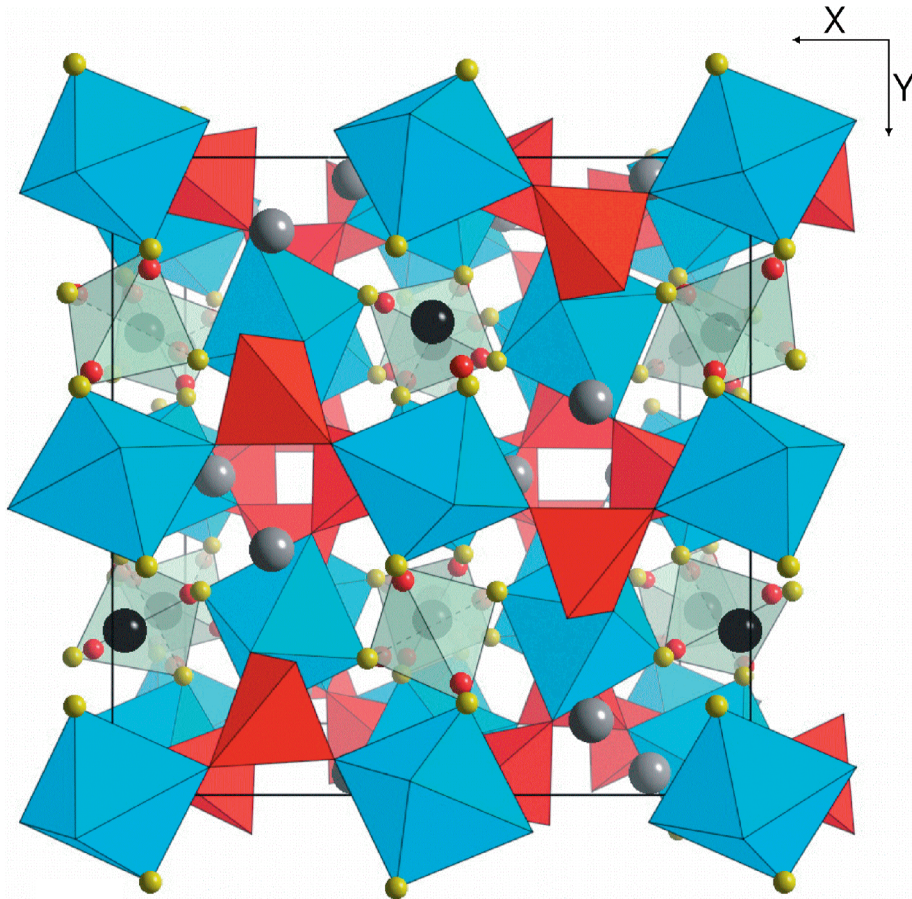


Fig. 3. The crystal structure of holtstamite projected along the c-axis. Blue and red polyhedra represent octahedral M1- and tetrahedral Si1-sites, respectively. Pale green polyhedra are H₄O₄ tetrahedra and small yellow and red filled circles show O₃- and H-atoms, respectively. Large filled circles in grey and black illustrate Ca1 and Ca2 cations, respectively.

Table 3. Atomic position parameters, occupancy factors and equivalent isotropic displacement parameters.

Atom	x	y	z	Occupancy	U_{eq}
M1	0	0	0	Mn0.503(6); Al0.497(6)	0.0106(3)
Ca1	0.3658(1)	0	1/4	1	0.0137(4)
Ca2	0	1/4	1/8	1	0.0151(4)
Si1	0.1180(1)	0	1/4	0.92(1)	0.0106(8)
Si2	1/2	1/4	1/8	0.11(1)	0.019(8)
O1	0.2930(3)	0.7167(2)	0.0979(3)	1	0.0165(7)
O2	0.1556(3)	0.5500(3)	0.0494(3)	1	0.0189(7)
O3	0.4442(3)	0.3586(3)	0.0222(3)	1	0.0186(8)
H	0.453(6)	0.333(6)	0.082(7)	1	0.04(2)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

In general, the atomic position parameters of holtstamite are very similar to those in henritermierite (Armbruster *et al.*, 2001). The refinement of the site occupancy of the M1 position (16c) yielded a mixture of about 50 % Mn and 50 % Al. A microprobe analysis of the investigated single crystal revealed a considerable amount of Fe. According to this analysis the occupation of the M1-site can be described as 47 % Al, 34 % Mn and 19 % Fe. This agrees very well with the site occupancy extracted from the X-ray data, which, however, do not allow discrimination of trivalent Fe and Mn.

Octahedrally coordinated Mn^{3+} at the M1-site in henritermierite displays a Jahn-Teller distortion of the tetragonal elongated type (Armbruster *et al.*, 2001). There are two short octahedron axes, O1-M1-O1 and O3-M1-O3, with M-O distances of 1.95 and 1.90 Å, respectively and one long axis, O2-M1-O2, with a M-O distance of 2.2 Å. In holtstamite, the M1-O distances of the short axes are similar to henritermierite, 1.94 and 1.89 Å. The substitution of Mn^{3+}

by Jahn-Teller inactive Al^{3+} and Fe^{3+} , however, leads to a considerable reduction of the M1-O2 distance (from 2.20 Å to 2.10 Å) and the distorted octahedron becomes more regular. The resulting octahedral axial ratio (1.085) for the M1-site is considerably smaller than in henritermierite (1.144). The M1-O2 bonds are almost parallel to the tetragonal *ab* plane (Fig. 4) and, thus, the lattice parameters do not change isotropically when going from henritermierite to holtstamite. As a consequence of the more regular MO_6 octahedra in holtstamite the Si1-O2 and Ca1-O2 distances in the latter are somewhat increased (Table 4).

The most conspicuous difference between henritermierite and holtstamite, apart from extensive Al-Mn³⁺ substitution at the M1-site, is the slightly cation deficient Si1-site

Table 4. Selected interatomic distances (Å) for holtstamite and henritermierite (Armbruster *et al.*, 2001) at 293 K.

	Holtstamite	Henritermierite
M1-O3 2x	1.894(3)	1.904(1)
M1-O1 2x	1.935(3)	1.952(1)
M1-O2 2x	2.101(3)	2.206(1)
M1-O (average)	1.977(3)	2.021(1)
Ca1-O3 2x	2.431(3)	2.445(1)
Ca1-O2 2x	2.427(3)	2.450(1)
Ca1-O1 2x	2.432(3)	2.476(1)
Ca1-O2 2x	2.486(3)	2.451(1)
Ca1-O (average)	2.444(3)	2.455(1)
Ca2-O3 4x	2.313(4)	2.333(1)
Ca2-O1 4x	2.606(3)	2.605(1)
Ca2-O (average)	2.460(4)	2.469(1)
Si1-O2 2x	1.651(3)	1.630(1)
Si1-O1 2x	1.654(3)	1.658(1)
Si1-O (average)	1.653(3)	1.644(1)
Si2-O3 4x	1.942(4)	1.982(1)
O3-H3	0.79(8)	0.75(3)
O2-H3	2.52(8)	2.21(3)
O3-O2	2.797(5)	2.763(1)
O3-O3	3.012(7)	3.095(1)
O3-O3 2x	3.249(7)	3.301(1)

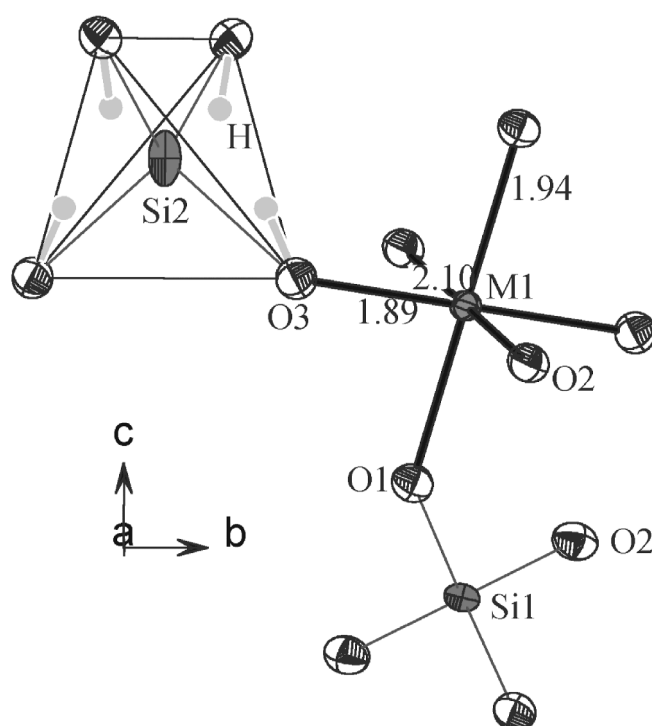


Fig. 4. The $M1O_6$ octahedron surrounded by $(O3H)_4$ and $Si1O1_2O_2$ in holtstamite. Hydrogen atoms are situated slightly above the $(O3H)_4$ tetrahedral faces. The centres of these tetrahedra (site 8a) are weakly occupied by Si2 (11 %). Displacement ellipsoids indicate 50 % probability. The ellipsoids of O3 are isotropic and do not indicate a split position as introduced by Armbruster *et al.* (2001) for henritermierite.

(16e) occupied to 92 % by Si, which implies that O2 and O1 coordinating these Si atoms may partly correspond to OH. The Si deficiency on the Si1-site is partly balanced by additional Si (Si2) at the centre of the (O3H)₄ tetrahedra (8a). The Si-content in holtstamite is according to the single-crystal refinement $1.84 + 0.11 = 1.95$ atoms per formula unit.

Single-crystal FTIR-spectra of holtstamite reveal a strong OH-stretching band at ~ 3480 cm⁻¹ and additional bands at ~ 3560 and ~ 3670 cm⁻¹ (Fig. 5). The prominent OH-stretching band occurs at distinctly lower wavenumbers than OH-stretching bands (3598 and 3662 cm⁻¹) observed in IR-spectra of cubic hydrogarnets (*e.g.* Anthauer & Rossman, 1998; Geiger *et al.*, 2000; Rossman & Aines, 1991). Compared to FTIR-spectra of the Mn³⁺-analogue henritermierite, which displays a strong OH-stretching band related to hydrogarnet substitution at 3432 cm⁻¹ (Armbruster *et al.*, 2001), the OH-stretching modes in holtstamite are shifted towards higher wavenumbers (Fig. 5). This is consistent with the observed increase of the O3-H...O2 distance from 2.76 Å in henritermierite (Armbruster *et al.*, 2001) to 2.80 Å in holtstamite. Based on the frequency-distance correlation by Libowitzky (1999) the OH-stretching mode in holtstamite is predicted to occur ~ 70 cm⁻¹ higher than in henritermierite. Taking into account differences in O3-H-O2 angles as well as H-O3 distances in the two mineral species this compares reasonably well with the observed shift of ~ 50 cm⁻¹. The band at ~ 3560 cm⁻¹ may be related to the side bands observed at ~ 3508 cm⁻¹ and ~ 3552 cm⁻¹ in the IR-spectra of henritermierite (Armbruster *et al.*, 2001). These side bands were interpreted by Armbruster *et al.* (2001) in terms of dynamic O-H orientations towards a remote O3 hydrogen bond acceptor or alternatively as an effect of different local environments.

An alternative interpretation of the FTIR-spectrum of holtstamite is that the bands at ~ 3480 and ~ 3560 cm⁻¹ represent OH-stretching bands related to (H₄O₄)-groups with different

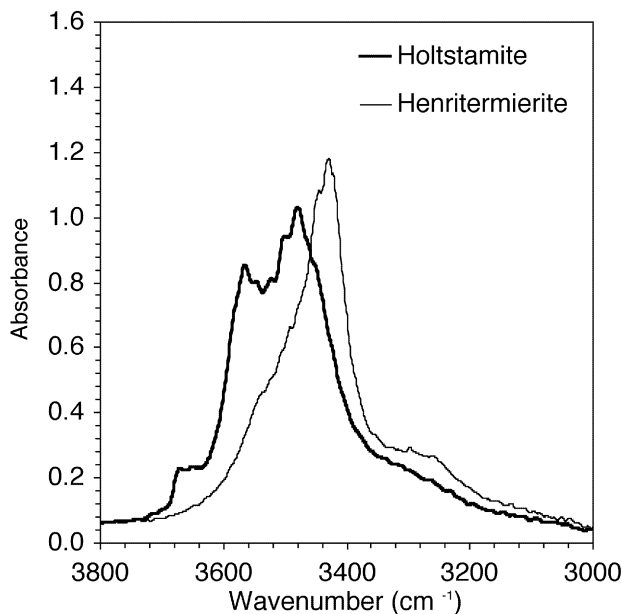


Fig. 5. Unpolarised FTIR-spectra of a 17 µm thick polished (001)-platelet of holtstamite (crystal WIR of Table 1) and a 19 µm thick (001)-section of henritermierite (crystal NIROS).

sets of neighbouring M1O₆ octahedra. This is consistent with the small difference in crystal field splitting parameter, $10Dq$, for Mn³⁺ recorded in optical absorption spectra of henritermierite and holtstamite (Hålenius, 2003), which indicate that Mn³⁺ $10Dq$ in holtstamite is only *ca.* 3 % higher than in henritermierite. Based on the mean M1-O distances in the two phases and the inverse fifth power relationship (*e.g.* Burns, 1993) an increase of the Mn³⁺ $10Dq$ value of *ca.* 11 % is predicted. The difference between expected and observed values suggests that Mn³⁺-centred M1O₆-octahedra are larger than Al³⁺-centred octahedra in holtstamite. This kind of structural relaxation is not uncommon in solid solution series involving Al-Mn³⁺ substitution (*e.g.*, Langer, 1999).

In FTIR-spectra of henritermierite (Fig. 5), no obvious counterpart to the low intensity band at 3670 cm⁻¹ in the holtstamite spectrum is observed. This band may be associated with the indicated structural relaxation, but may also be due to OH-stretching modes of hydrogen bonded to O2 or O1, *i.e.* related to the Si1-site. The cation deficiency at the Si1-site recorded in the structure refinement of holtstamite underlines this possibility.

Although, no direct determinations of OH-contents in holtstamite were possible due to sample character, FTIR-spectra (Fig. 5) indicate that OH-concentrations in holtstamite are of comparable order of magnitude to those in henritermierite. The calculated OH-content in analyses of holtstamite varies in a consistent manner, showing close to 4 (OH) pfu for henritermierite-rich compositions (crystal W1 of Table 2) and a gradual increase to ~ 4.7 (OH) pfu in the most Al-rich holtstamite crystals (*e.g.* crystals WIR and WOS of Table 2). The number of [SiO₄]-groups correlates inversely from ~ 2 pfu to ~ 1.8 pfu. Even within single crystals of holtstamite one can observe

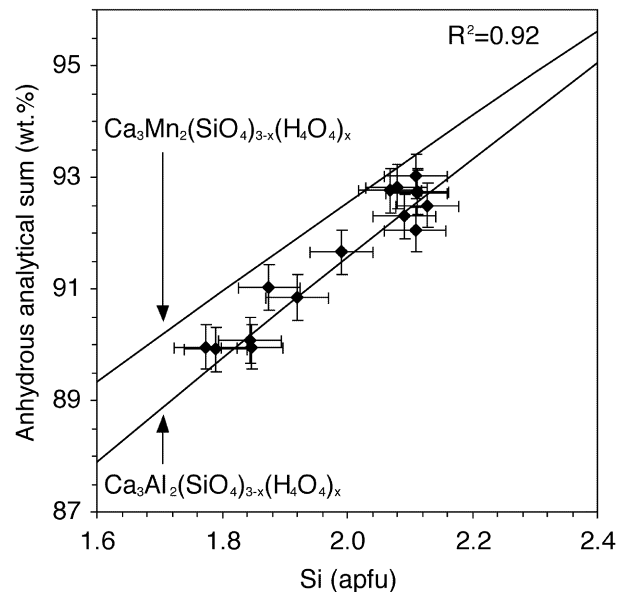


Fig. 6. Correlation plot of Si-contents and the analytical sums in microprobe analyses of holtstamite crystal WX1. Error bars represent the standard deviations obtained for the analyses of zones WX1A and WX1B in Table 1. A least-squares fit of the data yields a correlation coefficient of 0.92. The two solid lines representing calculated values for hydrogarnet substitution in henritermierite and its hypothetical Al-analogue are shown for comparison.

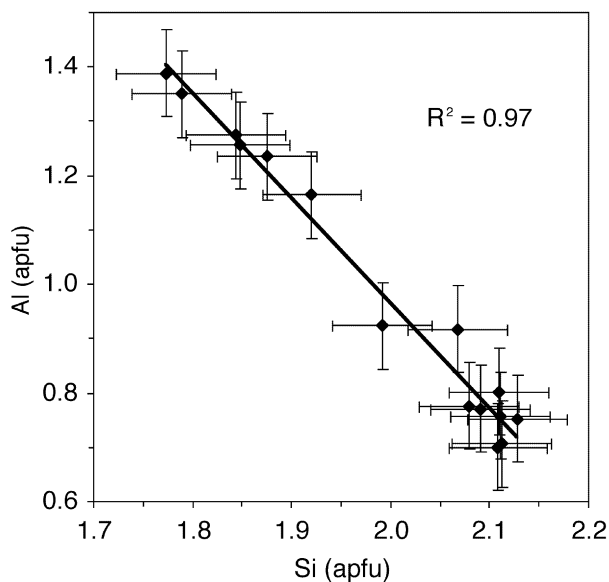


Fig. 7. Correlation plot of Si- and Al-contents in analyses of holtstamite crystal WX1. Error bars correspond to the standard deviations for analyses of Al and Si in zones 1 and 2 of WX1. A least-squares fit of the data yields a correlation coefficient of 0.97.

these patterns as demonstrated by, *e.g.*, the analyses of crystal WX1 (Fig. 6 and 7). This suggests that the simplified formula for holtstamite may be given in analogy with the cubic hydrogarnet hibschite as $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ rather than as $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_2(\text{OH})_4$.

Polarised single-crystal absorption spectra of holtstamite and henritermierite show strong absorption bands caused by spin-allowed d-d transitions in octahedrally coordinated Mn^{3+} (Hålenius, 2004) at ~ 12500 , ~ 19500 , ~ 21500 and $\sim 23000 \text{ cm}^{-1}$ (Fig. 8). The intensities of the absorption bands in spectra of a holtstamite crystal with the composi-

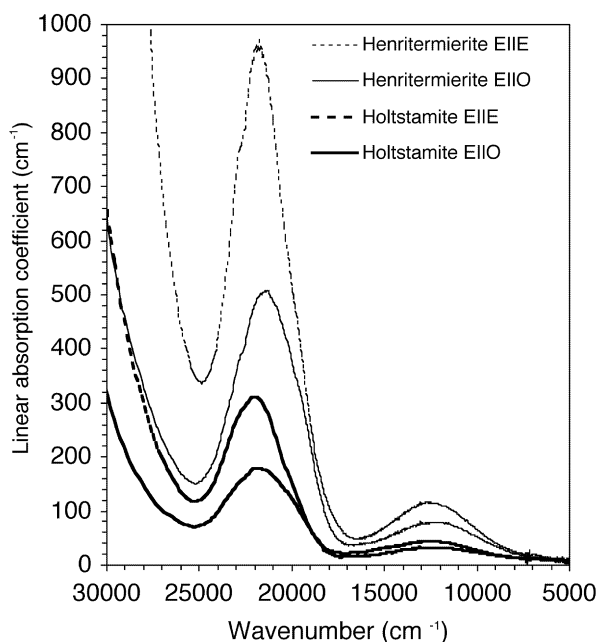


Fig. 8. Polarised optical absorption spectra of holtstamite (crystal WOS of Table 1) and henritermierite (crystal NIROS). The thickness of the measured crystals was 56 and 19 μm , respectively.

tion $\text{Ca}_{3.01}(\text{Al}_{1.28}\text{Mn}^{3+}_{0.64}\text{Fe}^{3+}_{0.08})_{\Sigma 2.00}(\text{SiO}_4)_{1.82}(\text{OH})_{4.71}$ are $\sim 32\%$ of those recorded for a henritermierite crystal from the N'Chwaning mine, South Africa, with the composition $\text{Ca}_{2.97}(\text{Mn}^{3+}_{1.97}\text{Al}_{0.04}\text{Fe}^{3+}_{0.01})_{\Sigma 2.02}(\text{SiO}_4)_{2.02}(\text{OH})_{3.91}$. This compares very well with an analytical Mn-ratio of 0.35 for these two crystals and it effectively demonstrates that Mn is present in the trivalent state in holtstamite as proposed by Hålenius (2004). In addition, bond distance data obtained from the structural refinement indicate that manganese as well as iron is present in the trivalent state in holtstamite.

The proposed simplified formula, $\text{Ca}_3(\text{Al}, \text{Mn}^{3+})_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$, of holtstamite includes trivalent manganese at the octahedral M1-site. The reason for choosing this formula rather than a proper end-member formula is based on the assumption that the tetragonal hydrogarnet structure is stabilised due to the presence of essential amounts of the Jahn-Teller distorted Mn^{3+} -cation. The amount of trivalent manganese required to stabilise this tetragonal phase still needs to be explored. An indication of the minimum Mn^{3+} -substitution threshold is the occurrence of a cubic Mn^{3+} -bearing (Mn^{3+} -occupancy at the octahedral site ~ 0.10) hydrous andradite at Wessels mine (Armbruster, 1995).

Conclusions

A new tetragonal hydrogarnet, holtstamite, which is the Al-dominant analogue of the Mn^{3+} -rich hydrogarnet henritermierite, has been found in a small vesuvianite sample from Wessels Mine, South Africa.

Trivalent manganese seems to be a necessary component to stabilise this tetragonal Al-dominant hydrogarnet with respect to the cubic counterparts. In combination with recorded variations in Si- and OH-contents in the present analyses we consequently propose that the mineral formula for holtstamite should be defined as $\text{Ca}_3(\text{Al}, \text{Mn}^{3+})_2(\text{SiO}_4)_{3-x}(\text{H}_4\text{O}_4)_x$ (with $\text{Al} > \text{Mn}^{3+}$) rather than $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_2(\text{OH})_4$.

The crystal field splitting parameter, $10Dq$, for Mn^{3+} in holtstamite shows a much smaller increase with respect to henritermierite than the differences in mean M1-O distances in the two phases suggest. This discrepancy is ascribed to structural relaxation, which is likely to be the reason for the more complex OH-stretching region in FTIR-spectra of holtstamite.

The relatively widespread occurrences of cubic hydrogarnet polymorphs as, *e.g.*, hibschite and the scarcity of tetragonal hydrogarnets in nature in combination with the fact that they are always Mn^{3+} -bearing suggest that the latter are stabilised by the presence of fractions of trivalent manganese. The holtstamite example suggests that additional Mn^{3+} -stabilised tetragonal hydrogarnets, *e.g.* "hydroandradite", may exist in nature.

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