Hjalmarite, a new Na–Mn member of the amphibole supergroup, from Mn skarn in the Långban deposit, Värmland, Sweden

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Abstract: Hjalmarite, ideally ^ANa^B(NaMn)^CMg₅^TSi₈O₂₂^W(OH)₂, is a new root-name member of the amphibole supergroup, discovered in skarn from the Långban Fe–Mn–(Ba–As–Pb–Sb–Be–B) deposit, Filipstad, Värmland, Sweden (IMA-CNMNC 2017-070). It occurs closely associated with mainly rhodonite and quartz. It is gravish white with vitreous luster and non-fluorescent. The crystals are up to 5 mm in length and display splintery fracture and perfect cleavage on {110}. Hjalmarite is colorless (nonpleochroic) in thin section and optically biaxial (-), with $\alpha = 1.620(5)$, $\beta = 1.630(5)$, $\gamma = 1.640(5)$. The calculated density is 3.12 Mg/m³. Average VHN₁₀₀ is 782, corresponding to ca. 5¹/₂ Mohs. An empirical formula, derived from electron-microprobe analyses in combination with crystal-structure refinements, is $(Na_{0.84}K_{0.16})_{\Sigma_1}(Na_{1.01}Mn_{0.55}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_5}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_5}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_5}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_5}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_5}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_5}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_5}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_5}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_5}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_5}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_5}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_5}Ca_{0.43}Sr_{0.01})_{\Sigma_2}(Mg_{3.83}Mn_{1.16}Al_{0.01})_{\Sigma_2}(M$ $(Si_{7.99}Al_{0.01})_{\Sigma_8}O_{22}(OH_{1.92}F_{0.08})_{\Sigma_2}$ An infra-red spectrum of hjalmarite shows distinct absorption bands at 3673 cm⁻¹ and 3731 cm⁻¹ polarized in the α direction. The eight strongest Bragg peaks in the powder X-ray diffraction pattern are [d (Å), I (%), (*hkl*)]: 3.164, 100, (310); 2.837, 50, (330); 8.50, 44, (110); 3.302; 40, (240); 1.670, 34, (461); 1.448, 32, (661); 2.727, 30, (151); 2.183, 18 (261). Single-crystal X-ray diffraction data were collected at 298 K and 180 K. The crystal structure at ambient temperature was refined in space group C2/m to R1 = 2.6% [$I > 2\sigma(I)$], with observed unit-cell parameters a = 9.9113(3), b = 18.1361(4), c = 5.2831(5) Å, $\beta = 103.658(5)^{\circ}$ and V = 922.80(9) Å³. The A and M(4) sites split into A(m) (K⁺, Na⁺), A(2) (Na⁺), and M(4') (Mn²⁺) subsites, respectively. Among the octahedrally coordinated C group cations, Mn²⁺ orders strongly at the M(2) site. No significant violation of C2/m symmetry or change in the structure topology was detected at low temperature (R1 = 2.1%). The hjalmarite-bearing skarn formed at peak regional metamorphism, $T \ge 600$ °C, at conditions of high SiO₂ activity and relatively low oxygen fugacity. The mineral name honors the Swedish geologist and mineralogist S.A. Hjalmar Sjögren (1856-1922).

Key-words: hjalmarite; amphibole supergroup; sodium-(magnesium-iron-manganese) subgroup; new mineral; crystal structure; Mn skarn; Långban; Sweden.

1. Introduction

The Långban Fe-Mn-(Ba-As-Pb-Sb-Be-B) deposit in the Filipstad district, Värmland, Sweden (59.86°N, 14.26°E, 215 m a.s.l.), is known for a bewildering richness in mineral species, with more than three hundred different species reported, and 73 type minerals described until today (Magnusson, 1930; Holtstam & Langhof, 1999; see also https://www.mindat.org). Despite extensive efforts to describe the various minerals of the deposit, not very much is known in detail about the different kinds of common skarn minerals such as garnet, pyroxene and amphibole that occur in significant amounts. Amphibole is a prevalent component of Mn skarn at Långban, and mainly consists of manganoan varieties in richterite or pargasite compositional space (e.g., Sundius, 1945; Holtstam, 1992; Oberti et al., 1993; Hålenius & Bosi, 2012). Christy & Gatedal (2005) recorded a rare Pb-bearing manganoan magnesio-hastingsite.

In a reconnaissance study of amphibole samples from the deposit, we have identified a new species, related to richterite $[{}^{A}Na^{B}(NaCa){}^{C}Mg_{5}{}^{T}Si_{8}O_{22}{}^{W}(OH)_{2}]$ via the homovalent substitution ${}^{[B]}Ca^{2+} \rightarrow {}^{[B]}Mn^{2+}$, which corresponds to "root name 13" in the current IMA nomenclature for the amphibole supergroup (Hawthorne *et al.*, 2012). It is the second recognized member of the sodium–(magnesium–iron–manganese) subgroup, after ferri-ghoseite. Sjögren (1891) described a physically similar, MnO-rich sample from Långban, named "astochit", but with higher CaO (5.83 wt%; from wet-chemical analysis) and lower Na2O (4.02 wt%) contents than found by us.

We have chosen the mineral name hjalmarite to honour the memory of S.A. Hjalmar Sjögren (1856–1922), a Swedish geologist and mineralogist who had broad geological interests, and was a pioneer in the mineralogical investigations of the Långban-type deposits in the Bergslagen region. As an appointed professor, Sjögren spearheaded the Geological Department at Uppsala University 1891–1894, and was curator at the Mineralogical Department, Swedish Museum of Natural History from 1901 until his death. He described the new mineral species adelite, retzian-(Ce), svabite, synadelphite and tilasite, and wrote the first overview of the Långban deposit intended for an international audience (Sjögren, 1910). Hjalmar Sjögren, "an elegant man of the world with typical sportsman habits" (Gavelin, 1938), was a prominent figure in Sweden around the turn of the nineteenth century, both within and outside academia, partly through his marriage to Anna Nobel (niece of the inventor Alfred Nobel). The mineral name is pronounced *YAL-MAR-AIT*. Note that "sjögrenite" of Frondel (1941) has been redefined as pyroaurite-2*H*.

The mineral and the mineral name have been approved by the International Mineralogical Association, IMA-CNMNC (2017–070). The holotype specimen, including a polished section, is deposited at the Swedish Museum of Natural History, Department of Geosciences, Box 50007, 10405 Stockholm, Sweden, under collection number GEO-NRM #g14150.

2. Occurrence and paragenesis

The Långban ores were extracted for iron (hematitemagnetite), manganese (braunite-hausmannite) and carbonate (dolomite) from 1711 to 1972. The Paleoproterozoic marble-hosted Långban-type (Moore, 1970) deposits in the Bergslagen ore region formed as chemical precipitates from volcanogenic hydrothermal solutions in a shallow submarine environment rich in oxygen (Boström *et al.*, 1979; Holtstam & Mansfeld, 2001). Deformed ore bodies, recrystallized skarn assemblages and several generations of cavity and fissure minerals attest to a subsequent complex geological development over the period 1.9–1.0 Ga.

Hialmarite occurs in dense Mn-rich skarn, as masses of irregularly arranged crystals associated mainly with rhodonite and quartz (Fig. 1). The grains are subhedral and commonly form 120° triple junctions with each other. Another type of amphibole, similar to the common brownish-yellow richterite normally found at Långban, occurs in a quartz-rich portion of the specimen, but not in direct contact with hjalmarite. Baryte is found as irregular grains up to 0.5 mm, commonly with inclusions of Ba-rich hedyphane (Fig. 2). In certain sections, serandite, a mineral previously not reported from Långban, is interstitial to hjalmarite, obviously as an alteration product of rhodonite (Fig. 2). Fine-grained pectolite sometimes occurs with serandite and as selvages between hjalmarite and quartz. In addition, bustamite and calcite were identified as minor constituents of the rock matrix.

Hjalmarite most probably crystallized during the main skarn-forming processes, coeval with Svecokarelian peak regional metamorphism in the area *ca.* 1.86 Ga ago, inferred at temperatures above 600 °C and moderate pressures of <3.5 kbar (Grew *et al.*, 1994; Christy & Gatedal, 2005) for the Långban deposit.



Fig. 1. The type specimen, GEO-NRM #g14150, with hjalmarite in darker grayish areas in the left and middle parts. Size *ca.* 12×8 cm.

(A)







Fig. 2. Field-emission backscatter-electron images of polished sections with hjalmarite (Hjm) associated with rhodonite (Rdn), quartz (Qtz), serandite (Ser), baryte (Brt), and pectolite (Pec). The black arrow on the upper image points to an inclusion of hedyphane. Note that the brightness/contrast level is slightly different between the two images.

3. Appearance and physical properties

Hjalmarite occurs as short-prismatic crystals $0.2-1 \times 1-5$ mm in size, and elongated in the [001] direction. Cleavage is perfect on {110} and fracture is uneven, splintery. The macroscopic color is gray-white and the luster vitreous; in thin section, hjalmarite is non-pleochroic and colorless. It is optically biaxial (–), with $\alpha = 1.620(5)$, $\beta = 1.630(5)$, $\gamma = 1.640(5)$ (measured in white light), $2V_{\text{meas}} = 60-70^\circ$, $2V_{\text{calc}} = 89.5^\circ$, Y = b and $Z \wedge c \sim 16^\circ$. The dispersion is moderate, r < v.

The mineral is non-fluorescent under both long- and short-wave ultraviolet light. Vickers hardness numbers were obtained using a Shimadzu type-M micro-hardness tester loaded with 100 g; an average of ten measurements (range 669–888) is 782, which corresponds to $5-5\frac{1}{2}$ on Mohs' scale. The experimentally obtained density (pycnometer) is 3.0(1) Mg/m³. Calculated values are 2.998 (ideal formula) or 3.123 Mg/m³ (empirical formula). The compatibility index obtained from Gladstone–Dale constants (Mandarino, 2007) is 0.025 (category: excellent).

4. Chemical composition

During reconnaissance, amphibole samples from Långban were analysed by energy-dispersive X-ray microanalysis; the present sample showed only K, Na, Ca, Mg, Si and Mn in significant amounts for elements with Z > 10. The precise composition was determined from point analyses on a polished surface using two electron probe microanalysers (EPMA) in wavelength-dispersive (WDS) mode: (A) an ARL-SEMQ (15 kV, 12 nA, beam size $1-2 \mu m$), with reference materials: (Na, Ca Mg, Al, Si) hornblendetype melt glass, K orthoclase, Fe hematite, Mn rhodonite, F topaz; (B) a JEOL 8200 Super Probe (WDS mode, 15 kV, 5 nA, 1 µm beam) with reference materials: Sr celestine, Mn rhodonite, K orthoclase, Pb galena, Fe fayalite, (Ca, Si, Al) grossular, Cr metal, Ni nickeline, Mg olivine, Ba sanbornite; the last round (B) of analyses were done on the crystal fragment used for the single-crystal study, see below. Results are given in Table 1. All Mn in hjalmarite is assumed to be Mn^{2+} ; even with small amounts of Mn^{3+} , richterite in the Långban deposit shows a distinct red-pink pleochroism related to d-d crystal-field transitions in Mn^{3+} . The presence of $(OH)^{-}$ is confirmed by Fourier-transform infrared (FTIR) spectroscopy and the crystal-structure refinements, as discussed below. Analyses of other light elements (Li, B, F) was done by nuclear-reaction analysis at the proton-beamline facility (LIBAF) at Lund University, Sweden (De La Rosa et al., 2017; Nilsson et al., 2017). The results are: Li 144 \pm 12 µg/g, B 33 \pm 3 µg/g and F 1820 \pm 200 μ g/g. The amount of these light elements is therefore almost negligible from a crystallographic point of view.

The chemical data suggest that variations between individual crystals of hjalmarite are rather small, but some Mg– Mn^{2+} replacement is indicated. The empirical formula is $(Na_{0.84}K_{0.16})_{\Sigma1}(Na_{1.01}Mn_{0.55}Ca_{0.43}Sr_{0.01})_{\Sigma2}(Mg_{3.83}Mn_{1.16})_{\Sigma2}$

Table 1. Chemical composition (wt.%) of hjalmarite from EPMA analysis.

Data set/point	A, n = 4	<i>■ B</i> 1	<i>B</i> 3	<i>B</i> 4	<i>B</i> 5	B, n = 4
SiO ₂	56.12	55.33	55.33	55.46	55.34	55.37
Al_2O_3	0.13	0.04	0.04	0.05	0.04	0.04
Cr_2O_3		0.02	0.01	0.00	0.03	0.01
Fe_2O_3	0.00	0.10	0.07	0.14	0.10	0.10
MnO	12.67	13.91	14.11	13.92	14.20	14.04
NiO		0.02	0.00	0.00	0.00	0.01
MgO	19.12	17.72	17.86	17.93	17.86	17.84
CaO	3.02	2.83	2.84	2.74	2.80	2.80
SrO		0.00	0.08	0.05	0.11	0.06
BaO		0.03	0.04	0.03	0.00	0.03
Na ₂ O	6.00	6.59	7.17	6.80	5.87	6.61
K ₂ O	1.10	0.88	0.84	0.84	0.90	0.86
PbO		0.20	0.23	0.43	0.23	0.27
F						0.18**
H_2O^*	1.99	2.07	2.08	2.08	2.07	2.08
O=F	-0.10	0.00	0.00	0.00	0.00	-0.07
Total	100.29	99.74	100.68	100.46	99.54	100.23
Formulae on						
24 (O,OH,F) basis						
Si	7.98	7.995	7.953	7.978	8.009	7.99
Al	0.01	0.006	0.006	0.008	0.006	0.01
Sum T cations	8.00	8.00	7.96	7.99	8.02	8.00
Al	0.00	0.00	0.00	0.00	0.00	0.00
Cr ³⁺		0.00	0.00	0.00	0.00	0.00
Fe ³⁺	0.00	0.01	0.01	0.01	0.01	0.01
Mg	4.06	3.82	3.83	3.84	3.85	3.83
Mn ²⁺	0.94	1.16	1.16	1.15	1.14	1.16
Ni ²⁺		0.01	0.00	0.00	0.00	0.00
Sum C cations	5.00	5.00	5.00	5.00	5.00	5.00
Mn ²⁺	0.59	0.54	0.56	0.55	0.60	0.55
Ca	0.46	0.44	0.44	0.42	0.43	0.43
Na	1.66	1.85	2.00	1.90	1.65	1.85
K	0.20	0.16	0.15	0.15	0.17	0.16
Pb		0.01	0.01	0.02	0.01	0.01
Ba		0.00	0.00	0.00	0.00	0.00
Sr		0.00	0.01	0.00	0.01	0.01
Sum $A + B$ cations	s 2.91	3.00	3.17	3.04	2.86	3.01
F	0.11					0.08
OH	1.89	2.00	2.00	2.00	2.00	1.92
Sum W cations	2.00	2.00	2.00	2.00	2.00	2.00

Note: A and *B* represents the two analytical sessions and instruments mentioned in the text. Ti and Cl was below detection in all points. Calculated from the structural formula.

**From nuclear-reaction analysis.

 $\begin{array}{l} Al_{0.01} \sum_{\Sigma 5} (Si_{7.99} Al_{0.01}) \sum_{\Sigma 8} O_{22} (OH_{1.92} F_{0.08}) \sum_{\Sigma 2} . The ideal formula for hjalmarite is {}^{A} Na^{B} (NaMn)^{C} Mg_{5}^{-T} Si_{8} O_{22}^{-W} (OH)_{2}, \mbox{ which requires Na}_{2} O \ 7.44\% \ MnO \ 8.52\%, \ MgO \ 24.19\% \ SiO_{2} \ 57.69, \ H_{2} O \ 2.16, \ total \ 100.00 \ wt\%. \end{array}$

5. Infra-red spectroscopy

Polarised single-crystal FTIR-spectra in the range 2000– 8000 cm⁻¹ were collected at a spectral resolution of 2 cm⁻¹ from a 35 μ m thick doubly polished single-crystal fragment oriented parallel (010), with a Bruker Vertex 70 spectrometer attached to a Bruker Hyperion 2000 IR-microscope. The spectra (Fig. 3) show distinct absorption bands at 3673 cm⁻¹ and 3731 cm⁻¹ in the α direction, with some shoulder features, caused by O–H stretching vibrations of

 $d_{\rm obs}$ (Å)

Fig. 3. Polarized single-crystal FTIR spectra of hjalmarite. Stippled curves indicate fitted bands. Sample thickness is 35 μ m. The spectra are vertically off-set for clarity.

the OH dipole at the O(3) position. The two main bands are typical for two local ^A \square -MgMgMg–SiSi and ^ANa– MgMgMg–SiSi atomic neareast- and next-nearest neighbor arrangements of cations around the O(3) atom, respectively, observed for richteritic amphibole compositions (see Hawthorne & Della Ventura, 2007). Spectral fitting (Fig. 3) using the PeakFit software reveals that the shoulder features are due to OH-bands at 3717 and 3664 cm⁻¹, and indicate also an additional weak band centred at 3779 cm⁻¹. The shoulder bands are likely due to ^A \square -MnMgMg–SiSi and ^ANa–MnMgMg–SiSi arrangements, as substitution of Mg by Mn²⁺ at *M*(1,3) is expected to cause a band shift of around -15 cm⁻¹ (*cf.* Reece *et al.*, 2002; Hawthorne & Della Ventura, 2007), whereas the cause of the weakest band at 3779 cm⁻¹ is unclear.

6. X-ray crystallography

6.1. Powder X-ray diffraction data

Data were recorded on a PANalytical X'Pert³ Powder diffractometer equipped with an X'celerator silicon-strip detector and operated at 40 mA and 45 kV (CuK α -radiation, $\lambda = 1.5406$ Å). Bragg peak positions were determined with the PANalytical HighScore Plus 4.6 software and corrected against an external Si standard (NBS 640b). Indexed *d* values and relative peak-heights above background are given in Table 2. The monoclinic unit-cell parameters, obtained by least-squares refinement of 28 reflections, are: a = 9.926(1)Å, b = 18.128(4) Å, c = 5.270(1) Å, $\beta = 103.74(3)^{\circ}$ and V = 921.1(1) Å³ for Z = 2.

6.2. Single-crystal X-ray diffraction data collection

The first single-crystal X-ray study was done at room temperature using an Oxford Diffraction Xcalibur diffractometer,

Note: The eight strongest Bragg reflections are in bold. Calculated intensities are from single-crystal diffraction data. Reflections with I < 4% are omitted.

operating at 50 kV and 30 mA, with monochromatized MoK α -radiation and equipped with a CCD detector put at a distance of 80 mm from the sample position. A combination of ω/ϕ scans, with a step scan width of 1° and exposure time of 15 s per frame at low θ angles and duplicating counting time at high θ angles, was used to maximize redundancy and data coverage. We collected high-resolution data (up to 0.5 Å). Data were processed with the program CrysAlis CCD, Oxford Diffraction Ltd., Version 1.171.33.41 (release 06–05–2009 CrysAlis171 .NET). Weak violations of C centering were observed, but the intensities were not strong enough to allow for a refinement in the space group $P2_1/m$ observed for synthetic Na(NaMg)Mg₅Si₈O₂₂(OH)₂ by Cámara et al. (2003). Therefore, a second data collection was done at 180 K using a Bruker APEX-II equipped with a CCD detector and an Oxford Cryosystem cryostat fluxing N₂. The temperature was lowered at a rate of 60 K/h. Four set of 180° ω scans, with step scan 0.5° and exposure time 20 s per frame were acquired. Data were processed with the same software as for the previous set. The lowtemperature data did not showed any evident violations of C centering.

The structure model was refined starting from the atom coordinates of crystal MR(4) (a manganoan richterite) of Oberti *et al.* (1993). Scattering curves for fully ionised



9.07	9.06	5	16	0	2	0
8.50	8.51	44	61	1	1	0
4.53	4.53	8	19	0	4	0
4.26	4.26	10	6	2	2	0
3.414	3.409	14	81	1	3	1
3.302	3.301	40	54	2	4	0
3.164	3.165	100	65	3	1	0
2.984	2.978	11	36	2	2	1
2.837	2.837	50	12	3	3	0
2.742	2.738	9	32	3	3	1
2.727	2.724	30	100	1	5	1
2.605	2.601	11	48	0	6	1
2.530	2.523	10	72	$\overline{2}$	0	2
2.405	2.405	10	5	3	5	0
2.344	2.343	11	30	3	5	1
2.332	2.333	7	14	$\overline{4}$	2	1
2.305	2.303	5	21	ī	7	1
2.183	2.181	18	43	2	6	1
2.071	2.071	5	1	0	8	1
2.043	2.041	5	11	3	5	1
1.917	1.918	17	8	5	1	0
1.8372	1.8374	17	7	4	4	2
1.6704	1.6698	34	16	4	6	1
1.6511	1.6507	6	6	4	8	0
1.6240	1.6236	7	6	1	11	0
1.6074	1.6072	10	3	6	0	0
1.5820	1.5824	5	1	6	2	0
1.5231	1.5256	5	2	1	9	2
1.5101	1.5103	9	11	2	6	3
1.4475	1.4480	32	35	6	6	1

Table 2. X-ray powder diffraction data for hjalmarite.

I(%)

 I_{calc} (%)

h

k

1

 d_{calc} (Å)

|--|

Temperature (K)	293(2)	180(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C2/m	C2/m
<i>a</i> (Å)	9.9113(3)	9.9046(10)
<i>b</i> (Å)	18.1361(4)	18.109(2)
<i>c</i> (Å)	5.2831(5)	5.2841(5)
β (°)	103.658(5)	103.7190(10)
Volume (Å ³)	922.80(9)	920.74(17)
Ζ	4	4
Density (calculated; Mg/m ³)	3.123	3.130
Absorption coefficient (mm^{-1})	0.894	0.927
<i>F</i> (000)	865	871
Crystal size (mm ³)	$0.10 \times 0.15 \times 0.50$	$0.10 \times 0.15 \times 0.50$
θ range for data collection	3.98 to 45.55°	2.25 to 31.61°
Index ranges	$-19 \le h \le 19$	$-13 \leq h \leq 14$
	$-36 \leq k \leq 36$	$-26 \leq k \leq 26$
	$-6 \le l \le 7$	$-7 \le l \le 7$
Reflections collected	19616	7247
Independent reflections	2061	1513
<i>R</i> (int)	0.0250	0.0260
Completeness to $\theta = 35.95^{\circ}$	99.2%	100.0%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2061/8/125	1513/8/125
Goodness-of-fit on F^2	1.065	1.024
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0261	R1 = 0.0214
	wR2 = 0.0565	wR2 = 0.0482
<i>R</i> indices (all data)	R1 = 0.0325	R1 = 0.0252
	wR2 = 0.0595	wR2 = 0.0505
Extinction coefficient	0.0037(3)	0.0002(2)
Largest diff. peak and hole (e $Å^{-3}$)	1.073	1.113
	-1.245	-1.000

chemical species were used at sites where chemical substitutions occur; neutral vs. ionized scattering curves were used at the T and anion sites [except O(3)]. The presence of splitting of scattering at the sites M(4) and A was observed and added to the model as M(4'), and A(m) and A(2) sites, respectively. The details of data collection and refinement results are reported in Table 3. Refined atom coordinates and equivalent isotropic-displacement parameters are reported in Table 4. Aniotropic refinements were carried out, and Tables S1 and S2 with anisotropic-displacement parameters are deposited with the journal and available as Supplementary Material linked to the journal at https:// pubs.geoscienceworld.org/eurimin. Selected interatomic distances and bond angles are given in Table 5. Site populations for hjalmarite at room temperature have been derived from the unit-formula and the results of the structure refinement (presented in Table 6). A $P2_1/m$ space group model, starting from the Cámara et al. (2003) atom coordinates, could be refined from low-temperature data yielding a good agreement (R1 = 3.13% for 1635 observed reflections $(F_{o} > 4\sigma F_{o})$ for a total of 3005 reflections. However, the geometry of the two symmetrically non-equivalent chains of tetrahedra was almost equal within standard deviations. The CIF file and observed and calculated structure factor lists are available as supplementary material in electronic form.

6.3. Results from crystal-structure refinement

There is an excellent agreement (Table 6) in ^CMn²⁺ contents between the refined site scattering values and the chemical analyses, 75.23 vs. 75.22 electrons per formula unit (*epfu*). On the basis of the observed mean bond lengths, and in agreement with what has been already observed by Oberti *et al.* (1993) for ^CMn²⁺, the following (strong) site preference is inferred: $M(2) \gg M(1) > M(3)$. This is similar to what is expected for ^CFe²⁺ according to present knowledge of amphibole crystal-chemistry (*cf.* the review in Oberti *et al.*, 2007). Enrichment of Mn²⁺ at M(2) is also shown by some very Mn-rich species such as mangano-ferri-eckermannite (formely "kôzulite"; Barkley *et al.*, 2010). Site assignments reported in Table 6 show that some Mn²⁺ is also present at the M(1) sites (a 10%), which is in agreement with the presence of shoulders shifted by *ca.* -15 cm⁻¹ with respect to the main absorption peaks in the IR spectrum.

The *A* cations are preferentially ordered, with 0.16 K apfu + 0.15 Na apfu at the A(m) site and Na at A(2/m) and A(2) sites (3.11 epfu and 3.82 epfu, respectively), accounting for 0.78 Na apfu, but also for the ordering of 0.01 apfu of Pb (Table 1) at the A(2)-sites, as observed for joesmithite (Moore, 1969; Moore *et al.*, 1993) and plumboan pargasite (Hålenius & Bosi, 2012). Accounting for Pb, the amount of Na by crystal-structure refinement is 0.71 apfu Na. The K and Na contents obtained by structure

Table 4. Refined atom coordinates and equivalent isotropic-displacement parameters.

Atom	T (K)	Site occupancy	x	у	z	$U_{\rm eq}$
O(1)	298	$O^0 0.21(5)$	0.11315(8)	0.08492(4)	0.2164(2)	0.00767(18)
. ,		O ⁻ 0.79(5)				
	180	$O^{0} 0.23(4)$ $O^{-} 0.77(4)$	0.11313(9)	0.08486(5)	0.21671(18)	0.00619(18)
O(2)	298	$O^{0} 0.26(5)$	0.12087(8)	0.16965(4)	0.7199(2)	0.00923(18)
- (-)		$O^- 0.74(5)$			•••••(-)	
	180	$O^0 0.09(4)$	0.12080(10)	0.16959(5)	0.71983(18)	0.00769(18)
O(3)	208	O = 0.91(4) $O^{-} = 0.86(3)$	0.10722(12)	0	0.7131(3)	0.0003(3)
0(3)	290	F^{-} 0.14(3)	0.10722(12)	0	0.7151(5)	0.0095(5)
	180	O ⁻ 0.83(3)	0.10700(14)	0	0.7131(3)	0.0078(4)
O(4)	202	$F^{-} 0.17(3)$	0.2(402(10)	0.24596(5)	0.7852(2)	0.01(5(2)
0(4)	298	$O^{-}0.73(5)$	0.30493(10)	0.24380(3)	0.7832(2)	0.0103(2)
	180	$O^0 0.31(4)$	0.36488(11)	0.24601(6)	0.7839(2)	0.0140(2)
	• • • •	$O^- 0.69(4)$	0.04505(0)			
O(5)	298	$O^{\circ} 0.33(5)$ $O^{-} 0.67(5)$	0.34537(9)	0.12911(5)	0.0802(2)	0.01136(19)
	180	$O^{0} 0.40(4)$	0.34589(10)	0.12979(5)	0.08247(18)	0.00861(18)
		O ⁻ 0.60(4)				
O(6)	298	$O^0 0.30(5)$	0.34297(9)	0.11500(5)	0.5812(2)	0.0131(2)
	180	$O^{0} 0.70(5)$ $O^{0} 0.36(4)$	0 34318(10)	0 11444(6)	0 58369(18)	0.01035(19)
	100	$O^- 0.64(4)$	0.54510(10)	0.11+++(0)	0.50505(10)	0.01055(17)
O(7)	298	$O^0 0.31(7)$	0.33852(12)	0	0.2801(3)	0.0129(3)
	190	$O^{-} 0.69(7)$	0.22005(1.4)	0	0.0770(2)	0.0104(2)
	180	$O^{-} 0.27(6)$	0.33883(14)	0	0.2779(3)	0.0104(3)
<i>T</i> (1)	298	$Si^0 0.59(3)$	0.27909(3)	0.084173(16)	0.28832(8)	0.00629(9)
	100	$Si^{4+} 0.41(3)$				
	180	$S1^{6} 0.62(3)$ $S1^{4+} 0.38(3)$	0.27928(4)	0.084186(18)	0.28917(7)	0.00505(9)
T(2)	298	$Si^0 0.61(3)$	0.28806(3)	0.169724(17)	0.79274(8)	0.00739(9)
		Si ⁴⁺ 0.39(3)				
	180	$Si^0 0.65(3)$	0.28827(4)	0.169773(19)	0.79338(7)	0.00591(9)
M(1)	298	$M\sigma^{2+} 0.912(4)$	0	0.08828(3)	1/2	0.0078(2)
<i>m</i> (1)	290	$Mn^{2+} 0.088(4)$	0	0.00020(3)	/ 2	0.0070(2)
	180	Mg_{2+}^{2+} 0.910(4)	0	0.08825(3)	1/2	0.0062(2)
M(2)	208	$Mn^{2+} 0.090(4)$ $Ma^{2+} 0.517(4)$	0	0.180722(10)	0	0.00876(12)
M(2)	298	$Mg^{2+} 0.483(4)$	0	0.180732(19)	0	0.00870(13)
	180	Mg^{2+} 0.508(4)	0	0.18053(2)	0	0.00690(13)
14(2)	200	$Mn^{2+} 0.492(4)$	0	0	0	0.00(0(2)
M(3)	298	$Mg^{-1} = 0.970(5)$ $Mn^{2+} = 0.030(5)$	0	0	0	0.0068(3)
	180	Mg^{2+} 0.961(5)	0	0	0	0.0057(3)
		$Mn^{2+} 0.039(5)$			1/	
M(4)	298	Na ⁺ 0.555(4)	0	0.27642(18)	1/2	0.0099(7)
	180	Na ^{$2+$} 0.546(5)	0	0.2700(5)	⁷ /2 1/2	0.021(3)
$M(4^{\prime})$	298	$Mn^{-1} 0.445(4)$ $Mn^{2+} 0.454(5)$	0	0.26436(14) 0.2677(2)	72 1/2	0.01/8(3)
$\Lambda(m)$	208	$K^+ 0.123(7)$	0.0283(10)	0.2077(2) 1/2	/ Z 0.083(3)	0.0137(8) 0.035(2)
A(m)	180	$K^+ 0.098(8)$	0.0265(10)	$\frac{1}{2}$	0.085(3) 0.072(3)	0.033(2) 0.024(3)
A	298	$Na^+ 0.283(14)$	0	1/2	0	0.021(3)
	180	$Na^+ 0.276(18)$	0	1/2	0	0.020
<i>A</i> (2)	298	$Na^+ 0.174(9)$	0	0.4748(5)	0	0.020(2)
	180	Na ⁺ 0.206(11)	0	0.4747(6)	0.0000	0.016(2)
Н	298	0.86(3)	0.191(5)	0	0.743(8)	0.035(12)
	180	0.83(3)	0.192(5)	0	0.746(8)	0.028(11)

Table 5. Selected interatomic distances (Å) and angles (°) in hjalmarite.

Т (К)	298	180	<i>T</i> (K)	298	180
T(1)-O(1)	1.598(1)	1.599(1)	T(2)–O(2)	1.610(1)	1.611(1)
T(1)–O(5)	1.627(1)	1.629(1)	T(2)-O(4)	1.582(1)	1.582(1)
T(1)–O(6)	1.626(1)	1.630(1)	T(2)-O(5)	1.679(1)	1.664(1)
T(1) - O(7)	1.641(1)	1.641(1)	T(2)-O(6)	1.663(1)	1.677(1)
< <i>T</i> (1)–O>	1.623	1.624	< <i>T</i> (2)–O>	1.633	1.634
$V(\text{\AA}^3)$	2.185	2.191	$V(\text{\AA}^3)$	2.220	2.222
TQE*	1.0028	1.0029	TQE*	1.0054	1.0053
TAV*	11.75	12.08	TAV*	22.94	22.51
$M(1)-O(1) \times 2$	2.074(1)	2.073(1)	$M(2)-O(1) \times 2$	2.231(1)	2.227(1)
$M(1)-O(2) \times 2$	2.075(1)	2.072(1)	$M(2)-O(2) \times 2$	2.122(1)	2.122(1)
$M(1)-O(3) \times 2$	2.097(1)	2.093(1)	$M(2) - O(4) \times 2$	2.034(1)	2.035(1)
< <i>M</i> (1)–O>	2.082	2.079	< <i>M</i> (2)–O>	2.129	2.128
<i>M</i> (3)–O(1) ×4	2.081(1)	2.079(1)	$M(4)-O(2) \times 2$	2.424(3)	2.330(8)
$M(3)-O(3) \times 2$	2.046(1)	2.045(1)	$M(4) - O(4) \times 2$	2.276(1)	2.253(2)
< <i>M</i> (3)–O>	2.070	2.067	$M(4) - O(5) \times 2$	2.932(2)	2.982(6)
			$M(4) - O(6) \times 2$	2.608(3)	2.704(8)
$A-O(5) \times 4$	2.884(1)	2.891(1)	< <i>M</i> (4)–O>	2.560	2.567
$A-O(6) \times 4$	3.169(1)	3.151(1)			
$A-O(7) \times 2$	2.423(1)	2.411(1)	$M(4')-O(2) \times 2$	2.253(3)	2.297(3)
<a-o></a-o>	2.906	2.899	$M(4')-O(4) \times 2$	2.247(1)	2.248(1)
			$M(4')-O(5) \times 2$	3.065(2)	3.008(3)
A(m)–O(5) ×2	2.959(7)	2.891(7)	$M(4')-O(6) \times 2$	2.776(3)	2.737(4)
A(m)–O(5) ×2	2.882(6)	2.876(9)	$<^{[6]}M(4')-O>$	2.426	2.429
A(m)–O(6) ×2	2.838(9)	2.855(10)	$<^{[8]}M(4')-O>$	2.586	2.573
A(m)–O(7)	2.355(9)	2.368(15)			
A(m)–O(7)	3.312(16)	3.377(15)	M(4') - M(4')	0.219(5)	0.042(10)
A(m)–O(7)	2.537(11)	2.523(17)			
<a(m)-o></a(m)-o>	2.844	2.851	$A(2)-O(5) \times 2$	2.465(2)	2.533(8)
			$A(2)-O(6) \times 2$	2.889(6)	2.870(6)
A(m) - A(2)	0.649(12)	0.615(12)	$A(2)-O(7) \times 2$	2.527(7)	2.455(2)
A(m)-A(m)	0.92(3)	0.82(3)	<a(2)–o></a(2)–o>	2.627	2.619
A - A(2)	0.46(1)	0.459(11)			
A - A(m)	0.461(14)	0.409(17)	A(2) - A(2)	0.91(2)	0.92(2)
T(1) - O(5) - T(2)	137.23(6)	136.96(7)	O(3)–H	0.81(5)	0.82(5)
T(1)-O(6)-T(2)	136.23(6)	135.92(7)	O(5)–O(6)–O(5)	168.89(5)	167.94(7)
T(1)-O(7)-T(1)	137.04(9)	136.59(10)	O(6)–O(7)–O(6)	105.68(8)	104.45(8)

*TQE, Mean quadratic elongation and the angle variance (TAV) (Robinson et al., 1971)

Table 6. Site populations for hjalmarite at room temperature.

Site	Site population (<i>apfu</i>)	Site scattering (epfu)		Mean bond length (Å)	
		Refined	Calculated	Refined	Calculated
<i>T</i> (1)	$3.98 \text{ Si}^{4+} + 0.02 \text{ Al}^{3+}$			1.623	1.620^{*}
T(2)	4 Si^{4+}			1.633	1.632^{*}
<i>M</i> (1)	$1.81 \text{ Mg}^{2+} + 0.19 \text{ Mn}^{2+}$	26.29	26.47	2.082	2.083^{**}
M(2)	$1.03 \text{ Mg}^{2+} + 0.96 \text{ Mn}^{2+}$	36.55	36.62	2.129	2.129^{**}
<i>M</i> (3)	$0.99 \text{ Mg}^{2+} + 0.01 \text{ Mn}^{2+}$	12.39	12.13	2.070	2.074^{**}
Σ C cations		75.23	75.22		
B cations	$1.01 \text{ Na} + 0.55 \text{ Mn}^{2+} + 0.43 \text{ Ca}^{2+} + 0.01 \text{ Sr}^{2+}$	34.46	33.84		
A cations W anions	0.84 Na ⁺ + 0.16 K ⁺ + 0.01 Pb ²⁺ 2.00 OH	11.62	13.01		

*Calculated using regression by Oberti et al. (2007); there is a close agreement between the refined values of site-scattering (epfu, electrons per formula unit) and mean bond-lengths (Å) and those calculated

(** using equations by Hawthorne & Oberti, 2007) based on the proposed site populations.

refinement (0.16 apfu K + 0.71 apfu Na) show the worst agreement with data obtained with the EPMA analysis (Na_{0.84}K_{0.16}), but this could be due to the complicated

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disordering at the A sites that may have hampered an accurate determination of the electron density at the A cavity. Alternatively, the Na content is overestimated in the chemical analyses of the crystal; this would be in agreement with the results from the FTIR spectra (Fig. 3), that suggest a non-negligible fraction of empty *A* cavities in hjalmarite. The existence of A(2) is related to the presence of divalent cations at the B sites. There is significant occupancy at the B-group sites by Mn^{2+} , which enters M(4'), displaced toward the strip of octahedra relative to the M(4) site, as already observed in manganoan richterite by Oberti *et al.* (1993).

The observed $\langle T(1)$ –O> distance is somewhat longer than what is expected from the small amounts of Al³⁺ estimated by EPMA analysis. The equation for calculating ^{*T*(1)}Al from $\langle T(1)$ –O> distance proposed by Oberti *et al.* (2007) yields 0.13 *apfu vs.* the analysed amount of 0.02 *apfu.* Similar values of $\langle T(1)$ –O> where reported by Oberti *et al.* (1993), although some of their crystals had slightly higher Al content. The observed $\langle T(2)$ –O> distance agrees with complete ^{IV}Si⁴⁺ occupancy of the *T*(2) site.

The low-temperature C2/m model showed reduction of the equivalent displacement parameters as well as a slight rotation (*ca.* 0.3–0.4°) of the internal angles of the double chain, confirming the absence of a hypothetical relaxation at low *T*. The main displacement is related to the coordinates of O(5) and O(6), and changes the bonding environment of the M(4) and *A* sites only very slightly. These displacements are further affected by a reduction of the distance between split sites due to the reduction of dynamic disorder related to the low temperature, which reduces the *A*–*A*(m) and M(4)-M(4)' distances (see Table 5).

The $P2_1/m$ space group model did not show differences within the standard deviations between the two chains of tetrahedra (for instance, the two kinking angles $O5A-O6A-O5A = 167.89(11)^{\circ}$ and O5B-O6B-O5B =167.92(11)° are almost equivalent). The differences compared to the average C2/m model are also lowest (Table 5). Any sensible phase transition should occur at <180 K, and must be second order in character. When considering the trend observed by Welch et al. (2007), that shows a decrease of transition temperature (T_c) with increasing average radius of the cations at the M(4) site (Table 1 in Welch et al., 2007), the composition ${}^{A}Na_{0.83}{}^{B}(Na_{0.83}Mg_{1.17}){}^{C}Mg_{5.00}Si_8O_{22}$ ${}^{W}(OH)_2$ (Cámara *et al.*, 2003) has $<^{[8]}r_{M(4)}> = 1.006$ (Å) and $T_c = 428$ K. The studied crystal of hjalmarite with ^B(Na_{1.01}Mn²⁺_{0.55}Ca²⁺_{0.43} Sr²⁺_{0.01}) has < ^[8] $r_{M(4)} > = 1.107$ (Å). The difference is significant but not enough to justify a $\Delta T_{\rm c} > 250$ K. Yet, the presence of 0.16 *apfu* of K at the A-sites of hjalmarite can have a strong effect in stabilizing the high-temperature topology.

7. Discussion

Hjalmarite obviously represent an unusual amphibole composition – globally as well as in the Långban-type deposits – despite the relatively few and common elements constituting it. It is unique among amphibole samples from Långban in being almost Fe-free, except for the "astochit" described by Sjögren (1891). Such a high Mn/Fe ratio is, however, attainable by the geochemical processes that led to initial Mn-enrichment in the pre-metamorphic progenitors of the Långban-type deposits (Holtstam & Mansfeld, 2001). The essential components Na₂O, MnO, MgO, SiO₂ and H₂O are available in abundance in many Mn skarns, so bulk composition alone cannot explain the rarity of this amphibole. Neither are the metamorphic conditions operative here in any way exceptional. Limitations of the amphibole crystal structure might thus be inferred for an explanation. Interestingly, Shau et al. (1993) reported an ^ANa- and ^CMg-rich amphibole with overall B-group composition (Na_{0.93}Mn_{0.66} $Ca_{0,41}$), *i.e.*, in essence a hjalmarite composition, from a metamorphosed Mn-deposit (Tirodi, Madhya Pradesh, India). Their sample exhibited frequent submicroscopic exsolution lamellae, indicating that the original amphibole composition was stable only at higher temperatures, consistent with the existence of a miscibility gap between the sodium amphiboles and the monoclinic magnesium-ironmanganese amphiboles. It is noteworthy that an amphibole with the A site dominantly empty was also described from the same locality, named "tirodite" by Dunn & Roy (1939), and characterized from a crystal structure point of view by Oberti & Ghose (1993). "Tirodite" was previously used to describe "manganocummingtonite"-like compositions without considering the amount of Na or the presence of Fe^{3+}/Al , and with Mn^{2+} dominant at the (B + C) sites and also at the B-sites only. Following the current IMA nomenclature for the amphibole supergroup (Hawthorne et al. 2012), mangano-cummingtonites are only those monoclinic magnesium-iron-manganese amphiboles that have Mn²⁺ dominant at the C sites, the ones with Mn²⁺ dominant at the B sites deserve a new rootname $(\Box Mn_2^{2+}Mn_5^{2+}Si_8)$ O₂₂(OH)₂ corresponds to "mangano-rootname 3"). Later, the use of the name "tirodite" was discontinued and "parvowinchite" was introduced, according to the IMA Subcommission on Amphibole Classification (Leake et al., 2004) without any further consideration. Recently, the name was changed once again, to ferri-ghoseite (\Box (NaMn²⁺) (Mg₄Fe³⁺)Si₈O₂₂(OH); IMA 12-F, Williams et al., 2013). This mineral is thus related to hjalmarite by the substitution ${}^{A}Na + {}^{M(2)}Mg \rightarrow {}^{A}\Box + {}^{M(2)}Fe^{3+}$. While Oberti & Ghose (1993) assigned some Mg to the M(4') site of ferri-ghoseite, giving the formula $^{A}(Na_{0.30}K_{0.03})^{B}(Na_{0.87}Ca_{0.39}Mn_{0.57}Mg_{0.17})^{C}(Mg_{3.84}Fe^{3+}_{0.72}Mn^{2+}_{0.38}Li_{0.06})(Si_{7.88}Al_{0.12})O_{22}$ $F_{0.40}(OH)_{1.60}$, the higher scattering at the M(4') obtained by structure refinement of hjalmarite excludes Mg at this site, which would increase further the disagreement at the B sites and worsen the excellent agreement observed at the C sites (Table 6). Oberti & Ghose (1993) also report a $<^{[6]}M(4')$ -O > = 2.378 Å, which is shorter than obtained here (2.426 Å, Table 5), in agreement with the presence of a smaller divalent cation at M(4') in ferri-ghoseite. Furthermore, Oberti & Ghose (1993) noted a distortion of the M(4) environment due to the presence of small divalent cations, and reported that the difference between the longest and the shortest distances [M(4)-O(5) vs. (M(4)-O(4)] =0.674 Å was at that time the highest value in the CSCC amphibole crystal structures database (C.N.R., Pavia, Italy), and approached the values found for ferromagnesian amphiboles (1.302 Å in grunerite by Finger (1969), and 1.015 Å in manganoan cummingtonite (with 0.24 Ca apfu) by Ghose & Yang (1989). The value for the hjalmarite crystal at room-*T* is very close, 0.656 Å, indicating a similar configuration around the *B* site in both amphiboles. The low *A*-site occupancy probably did not show any split electron density at the A(2) site, as these were not reported by Oberti & Ghose (1993). It is possible that hjalmarite is metastable at ambient conditions, but this would obviously depend on the exact B-group composition, specifically the Ca content, as well as the *A*-site occupancy.

While hjalmarite–quartz–rhodonite is interpreted as an equilibrium assemblage formed at peak metamorphic conditions, serandite and pectolite crystallized at lower P-T in retrogressive stages. Since pectolite–serandite represent an isomorphic solid-solution series (Takéuchi *et al.*, 1976), here occurring with close to end-member compositions, we conclude that these two minerals are not synchronous either. No oxide phases are present in the paragenesis, so the oxygen fugacity during hjalmarite formation can only be estimated as low compared to other rock types in the Långban deposit where, for example, braunite and kentrolite are abundant.

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