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Heyerdahlite, $Na_3Mn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$, a new mineral of the astrophyllite supergroup from the Larvik Plutonic complex, Norway: Description and crystal structure

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ABSTRACT

Heyerdahlite, ideally $Na_3Mn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$, is a new astrophyllite-supergroup mineral from the Larvik Plutonic complex, Norway. Heyerdahlite was found in a nepheline-syenite pegmatite with albite, aegirine, hastingsite/magnesio-hastingsite, kupletskite, lorenzenite and pyrophanite. Heyerdahlite is colourless to pale brown, transparent and has a vitreous lustre. Mohs hardness is 3, $D_{\text{calc.}} = 3.245$ g/cm^3. Heyerdahlite is biaxial (+), $\alpha = 1.694(2)$, $\beta = 1.710(5)$, $\gamma = 1.730(5)$, $2V_{\text{meas.}} = 80(4)°$ and $2V_{\text{calc.}} = 84.5°$. Cleavage is perfect parallel to {001}. The empirical formula based on 32.18 (O + F) apfu is $(Na_{1.18}K_{0.68}Rb_{0.12}Cs_{0.01}Pb_{0.01})_{\Sigma 2}Na_{1.00}(Mn_{6.29}Zn_{0.23}Mg_{0.07}Zr_{0.04}Fe^{2+}_{0.03}Ca_{0.01}Na_{0.34})_{\Sigma 7.01}(Ti_{1.78}Nb_{0.17}Mg_{0.03}Zr_{0.02})_{\Sigma 2}(Si_{8.03}O_{24})O_2[(OH)_{3.92}F_{0.08}]_{\Sigma 4}F_{1.00}[(H_2O)_{1.18}\square_{0.82}]_{\Sigma 2}$, for Z = 1. Heyerdahlite is triclinic, space group $P\bar{1}$, $a = 5.392(2)$, $b = 11.968(4)$, $c = 11.868(4)$ Å, $\alpha = 112.743(8)$, $\beta = 94.816(7)$, $\gamma = 103.037(8)°$ and $V = 675.6(7)$ Å^3. The crystal structure was refined to $R_1 = 4.44\%$ for 3577 unique ($F_o > 4\sigma F$) reflections. In the crystal structure of heyerdahlite, there are four $^{[4]}T$ sites occupied by Si. The $^{[6]}D$ site is occupied mainly by Ti. The T_4O_{12} astrophyllite ribbons composed of SiO_4 tetrahedra and D octahedra constitute the H (Heteropolyhedral) sheet. In the O (Octahedral) sheet, there are four Mn-dominant $^{[6]}M(1–4)$ sites. Two H sheets and one central O sheet form the HOH block, and adjacent HOH blocks link via a common X^P_D anion of the two D octahedra. In the **I** (Intermediate) block between HOH blocks, there are two interstitial cation sites, *A* and *B*, and a W_A site, partly occupied by H_2O. The *A* site splits into two sites, $^{[12]}A(1)$ and $^{[6]}A(2)$, partly occupied by K and Na, respectively, with A(1)–A(2) = 0.754 Å. The aggregate content of the *A* site is ideally Na_2 apfu. The $^{[10]}B$ site is occupied by Na. The W_A site is ideally occupied by $(H_2O)_2$ pfu. The mineral is named after the Norwegian explorer Thor Heyerdahl (1914–2002), who was born in Larvik.

Keywords: heyerdahlite, new mineral, astrophyllite supergroup, Larvik Plutonic complex, electron microprobe analysis, crystal structure, FTIR spectroscopy.

Introduction

Heyerdahlite, ideally $Na_3Mn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$, is a new astrophyllite-supergroup mineral from the Larvik Plutonic complex, Norway. The mineral is named heyerdahlite (pronunciation is HEY-AIR-DAL-'AIT) after the Norwegian explorer Thor Heyerdahl (1914–2002), who was born and raised in the city of Larvik, which is within the Larvik Plutonic complex. The new mineral species and its name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2016-108). The holotype specimen of heyerdahlite has been deposited in the collections of Royal Ontario Museum, Toronto, Ontario, Canada; the accession number is M57516. Here we report the description and crystal structure of heyerdahlite.

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The astrophyllite supergroup

General information on the astrophyllite supergroup (Sokolova *et al.*, 2017*a*), is given here to explain the site nomenclature and details of the structure used in the sections on infrared spectroscopy, chemical analysis and structure refinement below. The HOH block is the main structural unit in all astrophyllite-supergroup structures; it consists of three H–O–H sheets where the T_4O_{12} astrophyllite ribbons occur in the H sheets. In each structure, HOH blocks alternate with **I** (Intermediate) blocks along [001].

The general formula for the astrophyllite-supergroup minerals is of the form $A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O_{D2}X^O_{A4}X^P_{Dn}W_{A2}$, where C [cations at the *M*(1–4) sites in the O sheet] = Fe^{2+}, Mn, Na, Mg, Zn, Fe^{3+}, Ca, Zr and Li; D (cations in the H sheets) = $^{[6,5]}$Ti, Nb, Zr, Sn^{4+}, $^{[5]}Fe^{3+}$, Mg and Al; T = Si with minor Al; $A_{2p}B_rIW_{A2}$ (**I** block) where p = 1 or 2; r = 1 or 2; A = K, Cs, Ba, H_2O, Li, Rb, Pb^{2+}, Na and □; B = Na, Ca, Ba, H_2O and □; I represents the composition of the central part of the **I** block (excluding peripheral layers of the form $A_{2p}B_rW_{A2}$), e.g. $(PO_4)_2(CO_3)$ (devitoite); $X^O_D = O$; X^O_A = OH or F; X^P_D = F, O, OH, H_2O and □, where n = 0, 1 or 2 for $(X^P_D)_n$; $W_A = H_2O$ or □.

The thirteen minerals of the astrophyllite supergroup are divided into three groups based on (1) the type of self-linkage of HOH blocks, i.e. (a) HOH blocks link directly via $D–X^P_D–D$ bridges, or (b) HOH blocks do not link directly; and (2) the dominant cation of the O sheet [the C group: C_7 apfu (atoms per formula unit)]. In the astrophyllite group, HOH blocks connect via $D–X^P_D–D$ bridges, Fe^{2+} is dominant at C_7; in the kupletskite group, HOH blocks connect via $D–X^P_D–D$ bridges, Mn^{2+} is dominant at C_7; in the devitoite group, HOH blocks do not connect via $D–X^P_D–D$ bridges. The ideal structural formulae for the astrophyllite-supergroup minerals are given in Table 1.

Occurrence and mineral association

Heyerdahlite occurs in the Bratthagen nepheline syenite pegmatite of the Larvik Plutonic complex, Norway (Larsen 2010, 2013; Khomyakov *et al.*, 2011; Oberti *et al.*, 2014). The pegmatite is situated in a road cut on the main road RV8, ~200 m SE of the Bratthagen farm (59°09′26″N 10°00′39″E) in Lågendalen, Hedrum, Vestfold County, Norway.

The lardalite/foyaite rocks at Lågendalen contain the last segment of the Larvik Plutonic complex. The foyaites are younger than the lardalites and belong to the igneous rock complex of the Oslo region. The extreme mineral association in the Bratthagen syenite pegmatite shows mineralogical and geochemical features rather different from most of the syenite pegmatites in the Larvik Plutonic complex. Textural features suggest that these pegmatites are related to the host foyaite, which is younger than the lardalites. The mineral association is diagnostic of agpaitic pegmatites (Dahlgren, 2010). The locality has been protected by law since 1984, and mineral collecting is now prohibited.

Heyerdahlite formed as a late-stage hydrothermal mineral in a nepheline-syenite pegmatite. It occurs as radiating fans up to 2 mm in diameter, consisting of transparent colourless to pale-brown elongated lath-like crystals (Figs 1*a*,*b*). The heyerdahlite crystals are ~1 mm long and only 50 µm wide. Associated minerals are albite, aegirine, hastingsite/magnesio-hastingsite, kupletskite, lorenzenite and pyrophanite.

Almost 60 different species have been characterized in this area, many of which are typical of late-stage mineralization in highly evolved agpaitic intrusions (Oberti *et al.*, 2014).

Physical properties

Heyerdahlite is colourless to pale brown, it is transparent and has a vitreous lustre and a pale-brown streak. Cleavage is perfect parallel to {001}, heyerdahlite is brittle and has a hackly fracture. The Mohs hardness is 3. Heyerdahlite does not fluoresce under ultraviolet light. We did not measure density due to paucity of material, $D_{calc.}$ = 3.245 g/cm^3 (from the empirical formula). A spindle stage was used to orient a crystal for measurement of refraction indices and 2V by the extinction-curve method (Bartelmehs *et al.*, 1992). Heyerdahlite is biaxial (+), with refractive indices (λ = 589 nm) α = 1.694(2), β = 1.710(5), γ = 1.730(5); $2V_{meas.}$ = 80(4)° and $2V_{calc.}$ = 84.5°. The optical orientation was determined by transferring the crystal from the spindle stage to a single-crystal diffractometer and measuring the relative axial relations by X-ray diffraction; these values are given in Table 2. The dispersion is strong, $r > v$. It is pleochroic according to the scheme $X > Y > Z$, where X = yellowish brown, Y = brownish yellow and Z = pale yellow. The compatibility index (1 – Kp/Kc) = 0.028 (for $D_{calc.}$) is rated as excellent (Mandarino, 1981).

TABLE 1. Ideal structural formulae of the form $A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O_{D2}X^O_{A4}X^P_{Dn}W_{A2}$ for the astrophyllite-supergroup minerals*.

Mineral	Ideal structural formula													Ref.**
	A_2	B	C_7	D_2	$(T_4O_{12})_2$	I	X^O_{D2}	X^O_{A4}	X^P_D	W_{A2}	p	r	n	
Astrophyllite group														
Astrophyllite	K_2	Na	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	F		1	1	1	(1)
Niobophyllite	K_2	Na	Fe^{2+}_7	$(Nb,Ti)_2$	$(Si_4O_{12})_2$		O_2	$(OH)_4$	(O,F)		1	1	1	(1)
Zircophyllite	K_2	Na	Fe^{2+}_7	Zr_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	F		1	1	1	(2)
Tarbagataite	(K□)	Ca	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	(OH)		1	1	1	(3)
Nalivkinite	Li_2	Na	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	F	$(H_2O)_2$	1	1	1	(4)
Bulgakite	Li_2	(Ca,Na)	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	(O,F)	$(H_2O)_2$	1	1	1	(4)
Kupletskite group														
Kupletskite	K_2	Na	Mn^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	F		1	1	1	(5)
Niobokupletskite	K_2	Na	Mn^{2+}_7	$(Nb,Ti)_2$	$(Si_4O_{12})_2$		O_2	$(OH)_4$	(O,F)		1	1	1	(6)
Kupletskite-(Cs)	Cs_2	Na	Mn^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	F		1	1	1	(1)
Heyerdahlite	Na_2	Na	Mn^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	F	$(H_2O)_2$	1	1	1	(7)
Devitoite group														
Devitoite	Ba_4	Ba_2	Fe^{2+}_7	Fe^{3+}_2	$(Si_4O_{12})_2$	$(PO_4)_2(CO_3)$	O_2	$(OH)_4$	$□_2$		2	2	0	(8)
Sveinbergeite	$(H_2O)_2$	$[Ca(H_2O)]$	$(Fe^{2+}_6\ Fe^{3+})$	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	$[(OH)(H_2O)]$		1	2	2	(9)
Lobanovite	K_2	Na	$(Fe^{2+}_4\ Mg_2Na)$	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	□		1	1	0	(10, 11)

*After Sokolova *et al*. (2017*a*);

**References (the most recent work on the structure): (1) Cámara *et al*. (2010); (2) Sokolova and Hawthorne (2016); (3) Stepanov *et al*. (2012); (4) Agakhanov *et al.* (2016); (5) Piilonen *et al*. (2001); (6) Piilonen *et al*. (2000); (7) this work; (8) Kampf *et al*. (2010); (9) Khomyakov *et al*. (2011); (10) Sokolova and Cámara (2008); (11) Sokolova *et al*. (2017*b*).

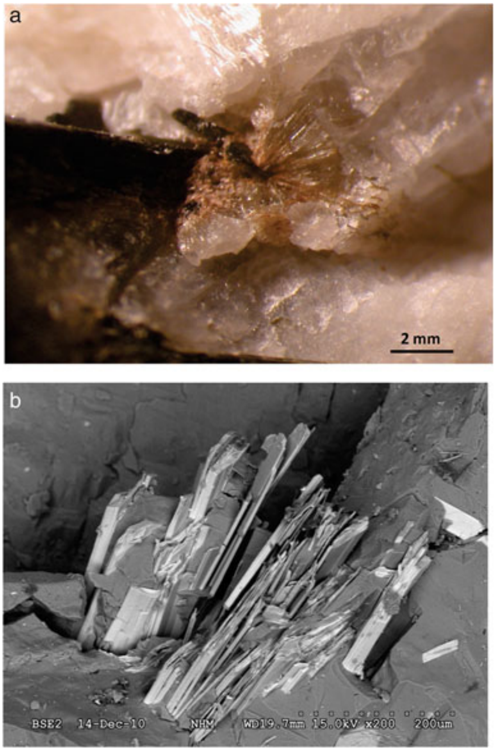

FIG. 1. (*a*) A fan of transparent colourless to pale-brown elongated crystals of heyerdahlite on albite, the black crystal is aegirine; (*b*) scanning electron microscopy image of heyerdahlite crystals.

Infrared spectroscopy

The Fourier-transform infrared (FTIR) spectra of heyerdahlite (Fig. 2) were collected on crystal fragments using a Bruker Hyperion 2000 IR microscope equipped with a liquid-nitrogen-cooled MCT detector (University of Manitoba). A single-crystal fragment was pressed into a homogenous film with a thickness of 10 μm with a diamond anvil and used to collect the powder spectrum shown in Fig. 2*a*. Single-crystal fragments with thicknesses of ~50 μm were used to collect the spectra shown in Figs 2*b* and 2*c*. Data over the range 4000–650 cm^{-1} were obtained by averaging 100 scans with a resolution of 4 cm^{-1}. Base-line correction was carried out using the *OPUS* spectroscopic software (Bruker Optic GmbH).

TABLE 2. Optical orientation (°).

	a	*b*	*c*
X	89.9	23.9	95.1
Y	86.5	110.1	9.8
Z	3.5	102.0	98.3

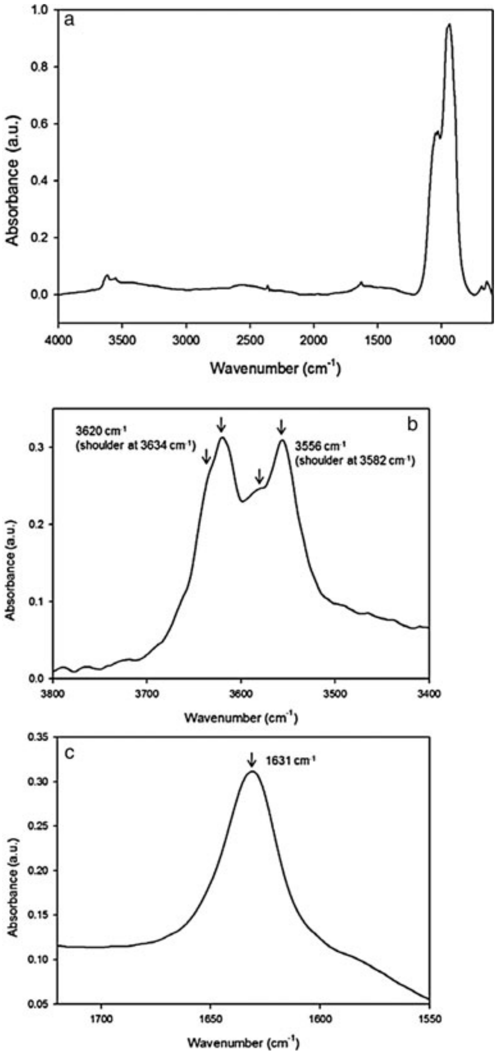

FIG. 2. FTIR spectra of heyerdahlite collected on (*a*) powder and (*b*,*c*) a single crystal.

In the powder (Fig. 2*a*) and single-crystal (Figs. 2*b*,*c*) FTIR spectra, two strong OH bands are observed at ~3620 cm^{-1} (with a shoulder at ~3634 cm^{-1}) and ~3556 cm^{-1} (with a shoulder at

~3582 cm^{-1}) (Figs 2*a*,*b*). These two bands correspond to principal OH stretching bands where OH groups occur at the $X^{O}_{A}(1)$ and $X^{O}_{A}(2)$ sites. There is a sharp peak at ~1631 cm^{-1} (Fig. 2*c*) that may be assigned to an H–O–H bending mode of an H_2O group. The corresponding H_2O stretching bands are extremely broad (at ~3440 cm^{-1}) (Fig. 2*b*) and underlie the sharper OH-stretching bands. In the lower-frequency region (Fig. 2*a*), two strong bands at ~1040 and ~940 cm^{-1} may be assigned to symmetric and asymmetric Si–O stretches and a less intense, broad band at ~635 cm^{-1} (with shoulder at ~685 cm^{-1}) is due to an Si–O–Si deformation. Multiple low-intensity bands observed in the range 2380–2301 cm^{-1} are due to atmospheric CO_2 transitions (Fig. 2*a*).

Chemical analysis

A crystal of heyerdahlite was analysed with a Cameca SX-100 electron-microprobe (University of Manitoba) operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 15 nA, a beam size of 10 µm and count times on peak and background of 20 and 10 s, respectively. The following standards were used: Si and Ca: diopside; F: fluoro-riebeckite; Na: albite; Nb: $Ba_2NaNb_5O_{15}$; Fe: fayalite; Mn: spessartine; Zr: zircon; Ti: titanite; Pb: PbTe; Mg: forsterite; Zn: gahnite; Cs: pollucite; K: orthoclase; and Rb: Rb-leucite. Tantalum, Al, Sn and Cr were sought but not detected. Data were reduced using the φ(ρZ) procedure of Pouchou and Pichoir (1985). The chemical composition of heyerdahlite is the mean of 8 determinations and is given in Table 3. The amount of H_2O was calculated from structure refinement. Table 3 gives the empirical formula unit based on 32.18 (O + F) apfu, with constraints OH + F = 5 pfu and H_2O = 1.18 pfu: $(Na_{1.18}K_{0.68}Rb_{0.12}Cs_{0.01}Pb_{0.01})_{\Sigma 2}Na_{1.00}(Mn_{6.29}Zn_{0.23}Mg_{0.07}Zr_{0.04}Fe^{2+}_{0.03}Ca_{0.01}Na_{0.34})_{\Sigma 7.01}(Ti_{1.78}Nb_{0.17}Mg_{0.03}Zr_{0.02})_{\Sigma 2}(Si_{8.03}O_{24})O_2[(OH)_{3.92}F_{0.08}]_{\Sigma 4}F_{1.00}[(H_2O)_{1.18}\square_{0.82}]_{\Sigma 2}$ for $Z = 1$. The basis of 32.18 (anions + H_2O groups) for calculation of the empirical formula unit was derived from the structure-refinement results: 31 anions (the established basis for calculation of the formula unit for the astrophyllite and kupletskite groups of the astrophyllite-supergroup minerals, Piilonen *et al.*, 2003) plus 1.18 H_2O pfu. Note that 1.18 H_2O pfu at the W_A site is necessary to complete the coordination of $Na_{1.18}$ apfu at the *A*(2) site (see below).

TABLE 3. Chemical composition (wt.%) and unit formula* (apfu) for heyerdahlite.

Constituent		Atoms per formula unit			
Nb_2O_5	1.67	Si	8.03	Ti	1.78
ZrO_2	0.53			Nb	0.17
TiO_2	10.37	Mn	6.29	Mg	0.03
SiO_2	35.17	Na	0.34	Zr	0.02
PbO	0.22	Zn	0.23	ΣD	2.00
ZnO	1.34	Mg	0.07		
FeO	0.14	Zr	0.04	Na	1.18
MnO	32.50	Fe^{2+}	0.03	K	0.68
CaO	0.03	Ca	0.01	Rb	0.12
MgO	0.30	ΣM	7.01	Cs	0.01
Cs_2O	0.12			Pb	0.01
Rb_2O	0.82	Na(B)	1.00	ΣA	2.00
K_2O	2.33				
Na_2O	5.70	OH	3.92	$F(X^{P}_{D})$	1.00
F	1.49	F	0.08		
H_2O**	4.12	ΣX^{O}_{A}	4.00	$H_2O(W_A)$	1.18
F = O	–0.63				
Total	96.22				

*Unit formula calculated on 32.18 (O + F) apfu, with OH + F = 5 pfu and H_2O = 1.18 pfu; **calculated from the structure-refinement results.

X-ray data collection and structure refinement

X-ray data for heyerdahlite were collected from a twinned crystal with a single-crystal Bruker D8 three-circle diffractometer equipped with a rotating-anode generator (Mo$K\alpha$ radiation), multilayer optics and an APEX-II detector (University of Manitoba). Powder X-ray diffraction data were obtained by collapsing experimental data from the twinned crystal into two dimensions and are presented in Table 4. Details of data collection and structure refinement are given in Table 5. The intensities of reflections were collected with a frame width of 0.3° and a frame time of 6 s, and an empirical absorption correction (*TWINABS,* Sheldrick, 2008) was applied. *CELL_NOW* (Sheldrick, 2004) was used to obtain an HKLF5 file, and the Bruker *SHELXTL Version 5.1* was used for the refinement of the crystal structure in space group $P\bar{1}$ using the atom coordinates of zircophyllite (Sokolova and Hawthorne, 2016); coordinates of the A(2) and W_A atoms were taken from the difference-Fourier map. The crystal structure of heyerdahlite was refined to $R_1 = 4.44\%$. The twin law is 180° rotation around the real axis [120] and the twin ratio is 0.572(3):0.428(3). The occupancies of eight cation sites were refined with the following scattering curves: *M*(1–4) and *D* sites: Mn and Ti; *A*(1) and *A*(2) sites: K and Na; *B* site: Na; and the W_A site: O. We observed disorder of K and Na at the *A*(1) and *A*(2) sites, with K–Na = 0.754 Å. The refinement of the site occupancy for the *B* site converged to 1.0 and was fixed. At the last stages of the refinement, occupancies of the *A*(1), *A*(2) and W_A sites were fixed in accord with chemical composition (Table 3). Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). Final atom coordinates and equivalent displacement parameters are given in Table 6, selected interatomic distances and angles in Table 7, refined site-scattering values and assigned site-populations in Table 8, details of hydrogen bonding in Table 9 and bond-valence values for selected anions in Table 10. A list of observed and calculated structure factors, Crystallography Information File (CIF) and a table of anisotropic displacement parameters have been deposited as Supplementary material (see below).

TABLE 4. Powder X-ray diffraction data* for heyerdahlite.

$I_{est.}$	d_{calc} (Å)	*h*	*k*	*l*	$I_{est.}$	d_{calc} (Å)	*h*	*k*	*l*	$I_{est.}$	d_{calc} (Å)	*h*	*k*	*l*
100	10.745	0	0	1	65	2.594	1	3	0	18	1.666	0	$\bar{7}$	3
10	9.886	0	$\bar{1}$	1		2.586	1	$\bar{4}$	3	14	1.650	$\bar{1}$	$\bar{2}$	7
12	3.734	1	$\bar{2}$	2	33	2.496	$\bar{2}$	1	2		1.6494	$\bar{1}$	4	4
	3.732	$\bar{1}$	1	2	14	2.424	$\bar{1}$	4	1		1.6491	3	0	1
43	3.582	0	0	3	14	2.414	$\bar{1}$	$\bar{3}$	4		1.6470	0	$\bar{7}$	2
14	3.546	1	1	1	20	2.318	1	3	1		1.6450	0	$\bar{7}$	4
14	3.295	0	$\bar{3}$	3		2.317	2	$\bar{1}$	2	29	1.5820	3	$\bar{5}$	1
	3.295	$\bar{1}$	$\bar{1}$	3	10	2.308	1	$\bar{4}$	4		1.5816	$\bar{3}$	$\bar{2}$	2
10	3.117	$\bar{1}$	2	2	23	2.250	$\bar{2}$	1	3	18	1.5680	$\bar{3}$	5	0
10	3.054	1	$\bar{2}$	3	14	2.059	2	$\bar{1}$	3		1.5660	$\bar{3}$	$\bar{2}$	3
14	2.893	1	$\bar{3}$	3	10	1.791	0	0	6		1.5656	1	4	3
	2.888	1	1	2		1.787	1	3	3		1.5635	$\bar{3}$	$\bar{2}$	1
55	2.791	$\bar{1}$	$\bar{3}$	1	10	1.779	1	$\bar{4}$	6		1.5627	3	$\bar{5}$	2
	2.787	1	$\bar{4}$	2	18	1.763	2	$\bar{6}$	2					
29	2.686	0	0	4		1.759	$\bar{2}$	1	5					
42	2.663	$\bar{2}$	1	1		1.758	$\bar{2}$	$\bar{4}$	2					
						1.757	$\bar{2}$	$\bar{4}$	3					

*Powder data were obtained by collapsing the experimental data from the single-crystal experiment into two dimensions. The most intense reflection (001) was covered by the beam stop. Therefore intensity was taken from the calculated powder diffraction pattern and all intensities rescaled accordingly. Intensities with $I_{est.} < 10$ are not listed.

TABLE 5. Miscellaneous refinement data for heyerdahlite.

a (Å)	5.392(2)
b	11.968(4)
c	11.868(4)
α (°)	112.743(8)
β	94.816(7)
γ	103.037(8)
V (Å^3)	675.6(7)
Space group	$P\bar{1}$
Z	1
Reflections ($I > 10\sigma I$)	5374
Absorption coefficient (mm^{-1})	4.58
$F(000)$	638.5
$D_{\text{calc.}}$ (g/cm^3)	3.245
Second twin component (%)	42.8(3)
Crystal size (mm)	0.14 × 0.03 × 0.007
Radiation/monochromator	Mo$K\alpha$/graphite
2θ-range for data collection (°)	3.79–60.40
h	$-7 \leq h \leq 7$
k	$-16 \leq k \leq 15$
l	$0 \leq l \leq 16$
$R(\sigma)$ (%)	2.76
Reflections collected	29,899
Independent reflections	3993
$F_o > 4\sigma F$	3577
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$
Refined parameters	262
Final R(obs) (%)	
R_1 ($F_o > 4\sigma F$)	4.44
R_1 (independent refl.)	5.12
wR_1	11.36
wR_2	11.72
Highest peak, deepest hole (e Å^{-3})	1.31, –1.21
Goodness of fit on F^2	1.128

Structure description

In the crystal structure of heyerdahlite, there are four *T* sites occupied by Si (Table 6) and tetrahedrally coordinated by O atoms, with $<\text{Si–O}> = 1.624$ Å (Table 7). There is one Ti-dominant *D* site coordinated by five O atoms and an $\text{X}_\text{D}^\text{P}$ anion [$\text{X}_\text{D}^\text{P} = \text{F}_{1.00}$], with $<\text{D–}\phi>$ 1.962 Å ($\phi = \text{O}$, F); and its composition is $(\text{Ti}_{1.78}\text{Nb}_{0.17}\text{Mg}_{0.03}\text{Zr}_{0.02})$, ideally Ti_2 apfu (Table 7). There are four Mn-dominant *M* sites octahedrally coordinated by O atoms and OH groups (plus minor F) at the $\text{X}_\text{A}^\text{O}(1,2)$ sites (Tables 6–8), with $<\text{M}(1\text{–}4)\text{–}\phi> = 2.200\text{–}2.156$ Å ($\phi = \text{O}$, OH). These four *M* sites give $(\text{Mn}_{6.29}\text{Na}_{0.33}\text{Zn}_{0.23}\text{Mg}_{0.07}\text{Zr}_{0.04}\text{Fe}^{2+}_{0.03}\text{Ca}_{0.01})_{\Sigma 7}$, ideally Mn_7 apfu (Table 2). Details of hydrogen bonding involving H atoms of OH groups are given in Table 9. M(1–4) octahedra share common edges to form a trioctahedral O sheet. As in most astrophyllite-supergroup structures, the sizes of M octahedra follow the pattern M(1) > M(2) > M(3) > M(4) due to the different linkages of M octahedra and the polyhedra of the H sheets (Sokolova, 2012). The T tetrahedra share vertices to form the $\text{T}_4\text{O}_{12}(\text{Si}_4\text{O}_{12})$ astrophyllite ribbon along [100]. Astrophyllite ribbons and D octahedra share common vertices to form an H sheet. Two H and one O sheets form an HOH block identical to that in kupletskite (Fig. 3*a*). In the heyerdahlite structure, D octahedra share a common $\text{X}_\text{D}^\text{P}$ anion where $\text{X}_\text{D}^\text{P} = \text{F}$ (Tables 8,10).

TABLE 6. Atom coordinates and equivalent displacement parameters (Å^2) for heyerdahlite.

Atom	*x*	*y*	*z*	U_{eq}
M(1)	0.84915(13)	0.20477(11)	0.47536(7)	0.0110(2)
M(2)	0.27856(18)	0.06551(9)	0.48484(10)	0.0119(3)
M(3)	0.42152(19)	0.35065(9)	0.48036(10)	0.0119(3)
M(4)	0	½	½	0.0107(4)
D	0.07928(13)	0.08646(10)	0.19710(6)	0.0093(2)
T(1)	0.6788(4)	0.27171(15)	0.23029(17)	0.0102(3)
T(2)	0.8145(3)	0.54827(16)	0.25964(15)	0.0102(3)
T(3)	0.3800(3)	0.67861(17)	0.26241(14)	0.0106(3)
T(4)	0.5082(3)	0.93209(15)	0.23523(16)	0.0083(3)
A(1)	0.1307(12)	0.2633(4)	0.9946(5)	0.0413(7)
A(2)	0.0992(14)	0.1991(5)	0.9956(6)	0.0238(7)
B	½	0	0	0.0205(5)
O(1)	0.7293(9)	0.3177(5)	0.3807(5)	0.0122(9)
O(2)	0.1261(9)	0.3883(5)	0.5905(4)	0.0105(8)
O(3)	0.5558(7)	0.2514(5)	0.5879(3)	0.0129(7)
O(4)	0.5761(9)	0.0144(5)	0.3848(4)	0.0116(9)
O(5)	0.0748(8)	0.5956(4)	0.2101(5)	0.0163(9)
O(6)	0.2464(10)	0.0397(5)	0.8280(5)	0.0225(11)
O(7)	0.4278(9)	0.4107(4)	0.7905(4)	0.0160(9)
O(8)	0.1243(11)	0.8065(5)	0.8311(5)	0.0212(10)
O(9)	0.2621(10)	0.9580(5)	0.1736(5)	0.0212(10)
O(10)	0.2631(10)	0.6038(4)	0.8008(5)	0.0170(10)
O(11)	0.5720(11)	0.2189(4)	0.7968(5)	0.0185(10)
O(12)	0.3822(9)	0.1920(5)	0.1684(5)	0.0222(11)
X^O_D	0.1469(6)	0.1605(5)	0.3656(3)	0.0116(6)
X^O_A (1)	0.2993(9)	0.4668(5)	0.3995(4)	0.0125(10)
X^O_A (2)	0.9899(10)	0.1183(5)	0.5938(5)	0.0160(10)
X^P_D	0	0	0	0.0154(7)
W_A	0.156(3)	0.3853(12)	0.0026(15)	0.059(3)*
H(1)	0.300(14)	0.431(6)	0.3102(17)	0.01503*
H(2)	1.067(14)	0.171(6)	0.682(2)	0.01920*

*U_{iso}.

In the **I** block between adjacent HOH blocks, there are two interstitial cation sites, *A* and *B*, and a W_A site partly occupied by H_2O. The *A* site splits into two sites, [12]-coordinated *A*(1) and [6]-coordinated *A*(2), separated by a short distance of 0.754 Å (Table 7). The *A*(1) site is coordinated by eleven O atoms and a F atom at the X^P_D site, and the *A*(2) site is coordinated by four O atoms, an X^P_D anion and an H_2O group at the W_A site. There is a short distance A(1)–W_A = 1.40 Å (Table 7) and hence the *A*(2) + W_A sites and the *A*(1) site cannot all be locally occupied. The *A*(1) and *A*(2) sites are occupied by ($\square_{1.18}K_{0.68}Rb_{0.12}Cs_{0.01}Pb_{0.01}$) pfu (41% occupancy) and ($Na_{1.18}\square_{0.82}$) pfu (59% occupancy), respectively (Table 8). As the *A*(1) site is occupied at 41%, the W_A site can be occupied by H_2O at 59%, i.e. by 1.18 H_2O pfu which is in accord with 1.18 Na apfu at the *A*(2) site (Table 8). A possible short-range-order arrangement of K and Na atoms where they fully occupy the *A*(1) and *A*(2) sites, respectively, is shown in Fig. 3*b*. The aggregate content of the *A* site is $(Na_{1.18}K_{0.68}Rb_{0.12}Cs_{0.01}Pb_{0.01})_{\Sigma 2}$, ideally Na_2 apfu. Note that the ideal composition of the *A* site, Na_2 apfu, (where it is fully occupied by Na) requires full occupancy of the W_A site: $(H_2O)_2$ pfu; otherwise the coordination of the Na atom is not complete. The [10]-coordinated *B* site is occupied by Na (Table 8), giving Na apfu.

Similar disorder at the *A* site was reported for the astrophyllite-group minerals bulgakite and nalivkinite (Agakhanov *et al.*, 2016) where the ideal composition of the *A* site is Li_2 apfu (Table 1) and nafertisite, ideally $Na_3Fe^{2+}_{10}Ti_2(Si_6O_{17})_2O_2(OH)_6F(H_2O)_2$ (Cámara *et al.*, 2014).

TABLE 7. Selected interatomic distances (Å) and angles (°) for heyerdahlite.

M(1)–(X^{O}_{D})a	2.181(3)	M(2)– X^{O}_{A}(2)c	2.134(5)	M(3)–O(1)	2.139(5)
M(1)–O(3)	2.185(4)	M(2)–O(4)	2.135(3)	M(3)–X^{O}_{A}(1)	2.151(5)
M(1)–O(2)a	2.186(5)	M(2)–X^{O}_{A}(2)b	2.155(6)	M(3)–O(2)	2.160(5)
M(1)–O(4)	2.200(5)	M(2)–O(3)	2.184(5)	M(3)–X^{O}_{A} (1)d	2.195(5)
M(1)–X^{O}_{A}(2)	2.220(6)	M(2)–O(4)c	2.281(5)	M(3)–X^{O}_{D}	2.230(5)
M(1)–O(1)	2.226(5)	M(2)–X^{O}_{D}	2.289(5)	M(3)–O(3)	2.230(3)
<M(1)–φ>	2.200	<M(2)–φ>	2.196	<M(3)–φ>	2.184
M(4)–X^{O}_{A}(1) x2	2.105(5)	T(1)–O(12)	1.606(5)	T(2)–O(10)d	1.612(4)
M(4)–O(1)b x2	2.173(5)	T(1)–O(8)d	1.608(5)	T(2)–O(2)d	1.611(5)
M(4)–O(2) x2	2.191(5)	T(1)–O(1)	1.629(5)	T(2)–O(5)a	1.636(5)
<M(4)–φ>	2.156	T(1)–O(10)d	1.639(4)	T(2)–O(7)d	1.639(5)
		<T(1)–O>	1.621	<T(2)–O>	1.625
T(3)–O(3)d	1.610(4)	T(4)–O(6)d	1.609(5)	T(1)d–O(10)–T(2)d	144.5(4)
T(3)–O(11)d	1.618(5)	T(4)–O(9)	1.609(5)	T(2)b–O(5)–T(3)	140.8(3)
T(3)–O(5)	1.641(5)	T(4)–O(4)e	1.622(5)	T(2)d–O(7)–T(3)d	140.5(3)
T(3)–O(7)d	1.644(5)	T(4)–O(11)d	1.639(4)	T(3)d–O(11)–T(4)d	144.7(4)
<T(3)–O>	1.628	<T(4)–O>	1.620	<T–O–T>	142.6
D–X^{O}_{D}	1.810(3)	A(1)–O(9)h	2.856(8)	A(2)–W_{A}l	2.15(1)
D–O(9)g	1.953(5)	A(1)–O(8)k	2.857(8)	A(2)–(X^{P}_{D})l	2.344(5)
D–O(6)f	1.955(5)	A(1)–O(12)l	2.869(7)	A(2)–O(9)h	2.477(8)
D–O(8)h	1.965(5)	A(1)–O(6)	2.886(8)	A(2)–O(8)k	2.484(9)
D–O(12)	1.969(5)	A(1)–(X^{P}_{D})l	3.097(4)	A(2)–O(12)e	2.491(8)
D–X^{P}_{D}	2.118(1)	A(1)–O(11)	3.464(8)	A(2)–O(6)	2.498(9)
<D–φ>	1.962	A(1)–O(11)b	3.464(8)	<A(2)–φ>	2.407
		A(1)–O(10)k	3.513(9)		
A(1)–A(2)	0.754(4)	A(1)–O(10)m	3.528(8)	B–O(6)c x2	2.614(5)
A(1)–W_{A}a	1.40(1)	A(1)–O(5)h	3.680(7)	B–O(12) x2	2.645(6)
		A(1)–O(7)	3.772(7)	B–O(9)g x2	2.664(5)
		A(1)–O(7)m	3.806(7)	B–O(8)d x2	2.664(6)
		<A(1)–φ>	3.316	B–X^{P}_{D} x2	2.696(2)
				<B–φ>	2.657

*φ = O, OH, F.

Operators for generating equivalent atoms: a: $x+1, y, z$; b: $x–1, y, z$; c: $–x+1, –y, –z+1$; d: $–x+1, –y+1, –z+1$; e: $x, y+1, z$; f: $–x, –y, –z+1$; g: $x, y–1, z$; h: $–x, –y+1, –z+1$; k: $–x, –y+1, –z+2$; ; l: $x, y, z+1$; m: $–x+1, –y+1, –z+2$.

The ideal formula of heyerdahlite

For the ideal structural formula of heyerdahlite of the form $A_2BC_7D_2(T_4O_{12})_2X^{O}_{D2}X^{O}_{A4}X^{P}_{D}W_{A2}$ (Sokolova *et al.*, 2017*a*), we sum the ideal compositions of the following sites: $C_7 = Mn_7$; $D = [^6]Ti_2$; $T_4 = Si_4$; $A_2 = Na_2$; $B = Na$; $X^{O}_{D2} = O_2$; $X^{O}_{A4} = (OH)_4$; $X^{P}_{D} = F$, $W_{A2} = (H_2O)_2$ (Table 8). Hence the ideal structural formula of heyerdahlite is $Na_2NaMn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$, $Z = 1$; the ideal formula of heyerdahlite is $Na_3Mn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$.

Heyerdahlite and kupletskite are related by the following substitution ${}^{A}Na^{+}_{2} + {}^{W}(H_2O)_2 \leftrightarrow {}^{A}K^{+}_{2} + {}^{W}\square$.

Summary

Heyerdahlite, ideally $Na_3Mn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$, is a new mineral of the kupletskite group (astrophyllite supergroup). The formula of heyerdahlite is of the form $A_2BC_7D_2(T_4O_{12})_2O_2(OH)_4X^{P}_{D}W_{A2}$, where ideally $C_7 = Mn_7$ at the *M* (1–4) sites; $D_2 = Ti_2$; $T_4 = Si_4$; $A_2 = Na_2$; $B = Na$; $X^{P}_{D} = F$; $W_{A2} = (H_2O)_2$.

The heyerdahlite structure consists of HOH blocks which alternate with interstitial sites of the **I** block along [001]. The topology of the **I** block is the same as that in bulgakite and nalivkinite where Li is the dominant cation at the *A* site.

TABLE 8. Refined site-scattering values and assigned site-populations for heyerdahlite.

Site*	Refined site-scattering (epfu)	Site population (apfu)	Calculated site-scattering (epfu)	<Ct–φ>$_{\text{obs.}}$ (Å)**	Ideal composition (pfu)
Cations					
M(1)	48.9(2)	$Mn_{6.29}Na_{0.32}Zn_{0.23}Mg_{0.07}Zr_{0.04}Fe^{2+}_{0.03}Ca_{0.01}$		2.200	
M(2)	48.9(3)			2.196	
M(3)	51.2(3)			2.184	
M(4)	26.1(2)			2.156	
Σ*M*	175.1	$Mn_{6.29}Na_{0.32}Zn_{0.23}Mg_{0.07}Zr_{0.04}Fe^{2+}_{0.03}Ca_{0.01}$	171.09		Mn_7
D	47.4(2)	$Ti_{1.78}Nb_{0.17}Mg_{0.03}Zr_{0.02}$	47.29	1.962	Ti_2
$^{[12]}A(1)$	18.73	$\square_{1.18}K_{0.68}Rb_{0.12}Cs_{0.01}Pb_{0.01}$	18.73	3.316	
$^{[6]}A(2)$	12.98	$Na_{1.18}\square_{0.82}$	12.98	2.656	
Σ*A*(1,2)	31.71	$Na_{1.18}K_{0.68}Rb_{0.12}Cs_{0.01}Pb_{0.01}$	31.71		Na_2
$^{[10]}B$	11.00	$Na_{1.00}$	11.00	2.657	Na
Anions					
X^{O}_{D}		$O_{2.00}$			O_2
$^{[3]}X^{O}_{A}(1,2)$		$(OH)_{3.92}F_{0.08}$			$(OH)_4$
$^{[6]}X^{P}_{D}$		$F_{1.00}$			F
W_A		$(H_2O)_{1.18}\square_{0.82}$			$(H_2O)_2$

*coordination number is given for non-[6]-coordinated sites;
**Ct = cation, φ = O, OH, F, H_2O.

TABLE 9. Hydrogen bonding in heyerdahlite.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠DHA (°)
$X^{O}_{A}(1)$–H(1)···O(8)a	0.98(1)	2.98(7)	3.47(7)	113(5)
$X^{O}_{A}(1)$–H(1)···O(12)	0.98(1)	2.86(6)	3.53(8)	126(5)
$X^{O}_{A}(2)$–H(2)···O(6)b	0.98(1)	2.98(7)	3.53(8)	117(5)
$X^{O}_{A}(2)$–H(2)···O(9)c	0.98(1)	3.12(7)	3.51(8)	105(5)

a: $-x, -y+1, -z+1$; b: $x+1, y, z$; c: $-x+1, -y+1, -z+1$.

TABLE 10. Selected bond-valence values* for heyerdahlite.

Atom**	M(1–4)	D	A(1)	A(2)	B	Σ
X^{O}_{D}	0.99	0.90				1.89
$X^{O}_{A}(1)$	1.11					1.11
$X^{O}_{A}(2)$	1.05					1.05
X^{P}_{D}		$0.31^{\times2\rightarrow}$	$0.04^{\times2\rightarrow}$	$0.08^{\times2\rightarrow}$	$0.09^{\times2\rightarrow}$	1.04

* Bond-valence parameters (in valence units) are from Brown (1981).
** M = Mn; D = Ti; A(1) = K, 50% occupancy; A(2) = Na, 50% occupancy; B = Na; X^{O}_{D} = O; $X^{O}_{A}(1,2)$ = OH; X^{P}_{D} = F.

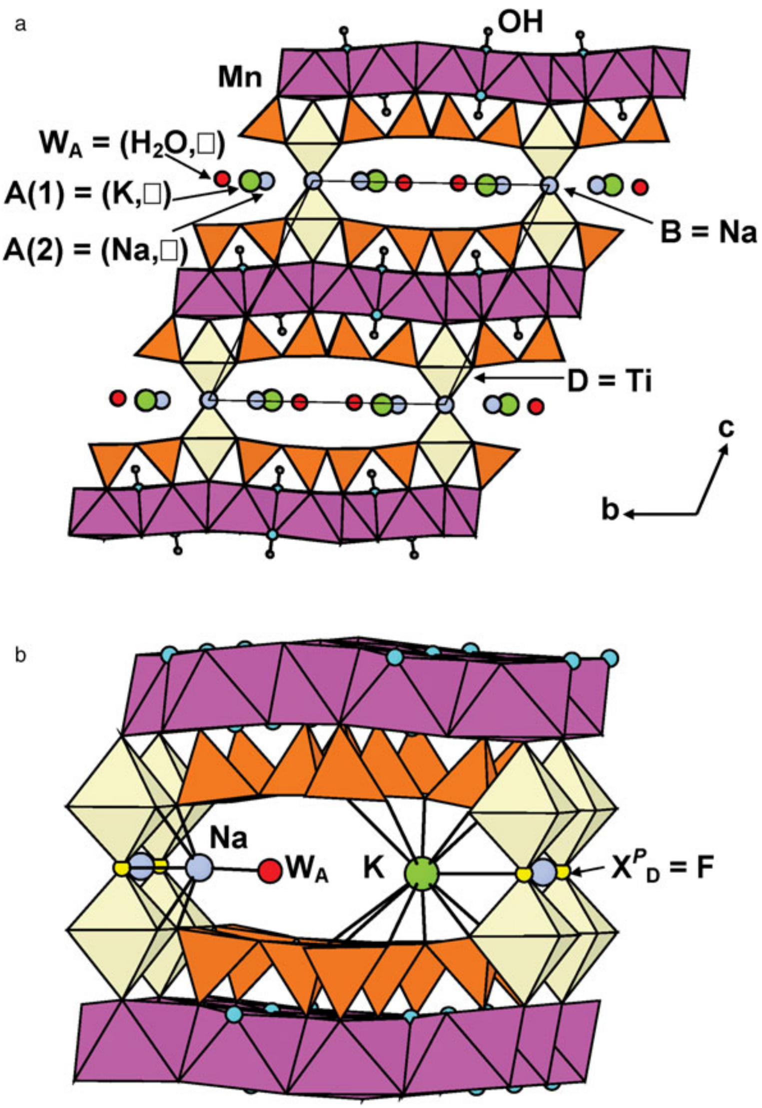

FIG. 3. The crystal structure of heyerdahlite: (*a*) general view; and (*b*) a possible short-range-order arrangement of K and Na atoms at the *A*(1) and *A*(2) sites, respectively. Mn-dominant and Ti-dominant octahedra are magenta and yellow, respectively; Si tetrahedra are orange; Na and K atoms at *B*, *A*(2) and *A*(1) sites are shown as medium blue and large green spheres; F atoms [X^P_D site], O atoms of OH groups [X^O_A sites] and H_2O groups [W_A site] are shown as small yellow, small turquoise and medium red spheres, respectively; H atoms of OH groups are shown as small grey spheres, O–H bonds are shown as black lines; the unit cell is shown with thin black lines.

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Supplementary material

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