

Sveinbergeite, $\text{Ca}(\text{Fe}_6^{2+}\text{Fe}^{3+})\text{Ti}_2(\text{Si}_4\text{O}_{12})_2\text{O}_2(\text{OH})_5(\text{H}_2\text{O})_4$, a new astrophyllite-group mineral from the Larvik Plutonic Complex, Oslo Region, Norway: description and crystal structure

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ABSTRACT

Sveinbergeite, $\text{Ca}(\text{Fe}_6^{2+}\text{Fe}^{3+})\text{Ti}_2(\text{Si}_4\text{O}_{12})_2\text{O}_2(\text{OH})_5(\text{H}_2\text{O})_4$, is a new astrophyllite-group mineral discovered in a syenite pegmatite at Buer on the Vesterøya peninsula, Sandefjord, Oslo Region, Norway. The mineral occurs in pegmatite cavities as 0.01–0.05 mm thick lamellar (0.2–0.5 × 5–10 mm) crystals forming rosette-like divergent groups and spherical aggregates, which are covered by brown coatings of iron (and possibly manganese) oxides, associated with magnesiokatophorite, aegirine, microcline, albite, calcite, fluorapatite, molybdenite, galena and a hochelagaite-like mineral. Crystals of sveinbergeite are deep green with a pale green streak and a vitreous and pearly lustre. Sveinbergeite has perfect cleavage on {001} and a Mohs hardness of 3. Its calculated density is 3.152 g/cm³. It is biaxial positive with α 1.745(2), β 1.746(2), γ 1.753(2), 2V(meas.) = 20(3)°. The mineral is pleochroic according to the scheme $Z > X \sim Y$: Z is deep green, X and Y are brownish green. Orientation is as follows: $X \perp (001)$, $Y \wedge b = 12^\circ$, $Z = a$, elongation positive. Sveinbergeite is triclinic, space group $P\bar{1}$, $a = 5.329(4)$, $b = 11.803(8)$, $c = 11.822(8)$ Å; $\alpha = 101.140(8)^\circ$, $\beta = 98.224(8)^\circ$, $\gamma = 102.442(8)^\circ$; $V = 699.0(8)$ Å³; $Z = 1$. The nine strongest lines in the X-ray powder diffraction pattern [d in Å(I)(hkl)] are: 11.395(100)(001,010), 2.880(38)(004), 2.640(31)($\bar{2}10, \bar{1}41$), 1.643(24)(0 $\bar{7}1, 0\bar{7}2$), 2.492(20)($\bar{2}\bar{1}1$), 1.616(15)(070), 1.573(14)($\bar{3}\bar{2}2$), 2.270(13)($\bar{1}\bar{3}4$) and 2.757(12)($\bar{1}40, \bar{1}\bar{3}2$). Chemical analysis by electron microprobe gave Nb₂O₅ 0.55, TiO₂ 10.76, ZrO₂ 0.48, SiO₂ 34.41, Al₂O₃ 0.34, Fe₂O₃ 5.57, FeO 29.39, MnO 1.27, CaO 3.87, MgO 0.52, K₂O 0.49, Na₂O 0.27, F 0.24, H₂O 8.05, O=F –0.10, sum 96.11 wt.%, the amount of H₂O was determined from structure refinement, and the valence state of Fe was calculated from structure refinement in accord with Mössbauer spectroscopy. The empirical formula, calculated on the basis of eight (Si + Al) p.f.u., is $(\text{Ca}_{0.95}\text{Na}_{0.12}\text{K}_{0.14})_{\Sigma 1.21}(\text{Fe}_{2.65}^{2+}\text{Fe}_{0.93}^{3+}\text{Mn}_{0.25}\text{Mg}_{0.18})_{\Sigma 7.01}(\text{Ti}_{1.86}\text{Nb}_{0.06}\text{Zr}_{0.05}\text{Fe}_{0.03}^{3+})_{\Sigma 2}(\text{Si}_{7.91}\text{Al}_{0.09})_{\Sigma 8}\text{O}_{34.61}\text{H}_{12.34}\text{F}_{0.17}$, $Z = 1$. The infrared spectrum of the mineral contains the following absorption frequencies: 3588, ~3398 (broad), ~3204 (broad), 1628, 1069, 1009, 942, 702, 655 and 560 cm⁻¹. The crystal structure of the mineral was solved by direct methods and refined to an R_1 index of 21.81%. The main structural unit in the sveinbergeite structure is an HOH layer which is topologically identical to that in the astrophyllite structure. Sveinbergeite differs from all other minerals of the astrophyllite group in the composition and topology of the interstitial A and B sites and linkage of adjacent HOH layers. The mineral is named in honour of Svein Arne Berge (b. 1949), a noted Norwegian amateur mineralogist and collector who was the first to observe and record this mineral from its type locality as a potential new species.

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Introduction

THE Larvik plutonic complex, situated in the southern part of the Oslo Region, Norway, is a large (more than 1000 km²) complex of larvikite–lardalite alkaline rocks, which is world-famous as a mineral province. At present, the complex is the type locality for about 30 minerals, and almost 200 mineral species are known to occur there; the majority of the new and rare minerals, as well as the mineral in question, were identified during investigations of highly mineralized syenite and nepheline syenite pegmatites (Raade *et al.*, 1980; Larsen, 2010).

Here we describe a new Ti silicate, sveinbergeite, named in honour of Svein Arne Berge (b. 1949) a noted Norwegian amateur mineralogist and collector from the town of Sandefjord, who has made a significant contribution to the mineralogy of alkaline pegmatites in the Larvik plutonic complex and who was the first to collect this mineral from the type locality in 1987. Sveinbergeite has already been recorded as a possible new species; it was briefly described as a murmanite-like hydrous Ca-Fe-Ti-silicate (sample UK-8; Engvoldsen *et al.*, 1991: pp. 30–31; Andersen *et al.*, 1996). The first analysis of the mineral was carried out by A. O. Larsen (Norsk Hydro Research Center), with UK-8 assumed to be a murmanite-like mineral. In 1992, S.A. Berge gave the holotype specimen of this mineral to APK for detailed study. It is difficult to exaggerate the difficulty of dealing with this material. Although initially the ‘crystals’ appeared to be large, up to 40 µm thick and 10 mm long, they were coated with iron oxide that had to be removed before measurements could be made. Underneath the coating, the crystals are fractured and deformed with wavy extinction, and diffract X-rays very poorly. Numerous crystals were examined before we found any which produced a diffraction pattern that could be indexed. We collected single-crystal X-ray intensity data on 5 crystals, and the crystal structure was refined for all of them. The information on the HOH layer was consistent in all five refinements, but the structure of the interlayer region was less well resolved, and therefore we present the refined structure only for the refinement with the lowest R_1 index. The

final R_1 index of the best refinement is 21.8%, which is much higher than is normally the case. However, it is sufficient to show that the general topological features of the structure are correct, and we present these results with the general philosophy that it is better to report imprecise results on such an interesting and unusual composition than no information at all. The presence of the coating was the reason why this material has remained as an unknown since its discovery in 1991. It was the work reported here that allowed Larsen (2010) to report UK-8 as an astrophyllite-group mineral.

The main structural unit in the crystal structure of sveinbergeite is an HOH layer which has the same topology and stereochemistry as the astrophyllite-group minerals: astrophyllite, nalivkinite, niobophyllite, kupletskite, niobokupletskite, and kupletskite-(Cs) (Cámara *et al.* 2010), with the general formula $A_2BC_7D_2(T_4O_{12})_2O_2(OH)_4X_{0-1}$, where $A = {}^{[13,12,5]}$ (dominant K, Cs, Li, minor Rb, Pb, Na, Ca and □); $B = {}^{[10]}$ (dominant Na, minor Ca); $C = {}^{[6]}$ (dominant Fe²⁺, Mn²⁺, minor Fe³⁺, Na, Mg, Ca, Li, Zr and Zn); $D = {}^{[5,6]}$ (dominant Ti, Nb and Zr, minor Sn, Ta and Mg); $T = {}^{[4]}$ (dominant Si, minor Al) and $X =$ dominant F, O, minor OH (modified from Piilonen *et al.*, 2003a and Cámara *et al.*, 2010) and devitoite, $[Ba_6(PO_4)_2(CO_3)]Fe_2^+Fe_3^+(Si_4O_{12})_2O_2(OH)_4$, (Kampf *et al.*, 2010). The topological character of the structural unit indicates sveinbergeite to be an astrophyllite-group mineral. However, the topology and stereochemistry of the interlayer block and linkage of HOH layers are different from all known structures in the astrophyllite group, adding further to the structural and chemical diversity of the HOH (Three-Layer Packet) minerals, which were pioneered by Belov (1963, 1976).

The new mineral species and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2010-027). The holotype specimen of sveinbergeite is deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Leninskii Pr. 18/2, 117071 Moscow, Russia, catalogue No. 3966. The catalogue numbers of the two cotype specimens of the mineral

deposited at the Natural History Museum, Section of Geology at the University of Oslo (Postboks 1172, Blindern, 0318 Oslo, Norway) are 42259 and 42260, respectively.

Occurrence and associated minerals

According to information supplied by S.A. Berge (pers. comm.) and published data (Engvoldsen *et al.*, 1991: pp. 30–31; Andersen *et al.*, 1996), the type locality of sveinbergeite is the Buer syenite pegmatite, which is situated on the Vesterøya peninsula, approximately 4.5 km south of the town of Sandefjord, Sandefjord municipality, Vestfold County, Norway. The locality is partly a road-cut and partly a natural outcrop where a large pegmatite, about $80 \times 2\text{--}8$ m, is exposed in larvikite. The pegmatite was blasted in 1987, when a new footpath and cycle track were being built. The pegmatite mainly consists of grey microcline crystals which are typically 2–5 cm across, with magnesiokataphorite, aenigmatite and aegirine as the dominant dark minerals. In a small part of the pegmatite, a eudialyte-group mineral forms masses which are 10–20 cm across. The pegmatite is rich in cavities in which sveinbergeite occurs associated with magnesiokataphorite, aegirine, microcline, albite, calcite, fluorapatite, molybdenite, galena, a hochelagaite-like mineral and gel-type coatings of amorphous iron and (manganese?) oxides. Sveinbergeite occurs in the cavities as dark green 0.01–0.05 mm thick lamellar (0.2–0.5 \times 5–10 mm) crystals forming rosette-like divergent groups and spherical aggregates (Fig. 1). It is also found as scaly, radiating bronze-brown masses. Other minerals found in the pegmatite are arsenopyrite, bastnäsité-(Ce), bertrandite, a biotite-group mineral, catapleiite, a chlorite-group mineral, elpidite, epididymite, goethite, hematite, heulandite-Ca, heulandite-K, magnetite, molybdenite, monazite-(Ce), montmorillonite, muscovite, opal, parisite-(Ce), pyrite, siderite, sphalerite, thorite, titanite and zircon.

Sveinbergeite is one of the latest of the pegmatite minerals to form. It is presumed to belong to the special genetic group of ‘transformation mineral species’ (Khomyakov and Yushkin, 1981; Khomyakov, 1996, 2008) which crystallized at a late stage of pegmatite formation through the hydration and decationation of an as yet unknown fully cationic mineral with an astrophyllite-like structure.

Physical and optical properties

Prior to recording information or physical data on sveinbergeite, the iron oxide coating was removed by physically abrading individual crystals (very gently) with a steel micro-blade. The main properties of sveinbergeite are presented in Table 1, where they are compared to those of astrophyllite. Crystals of sveinbergeite are deep green, with a pale green streak and a lustre that varies from vitreous to pearly. The mineral is opaque to transparent in thin flakes and does not

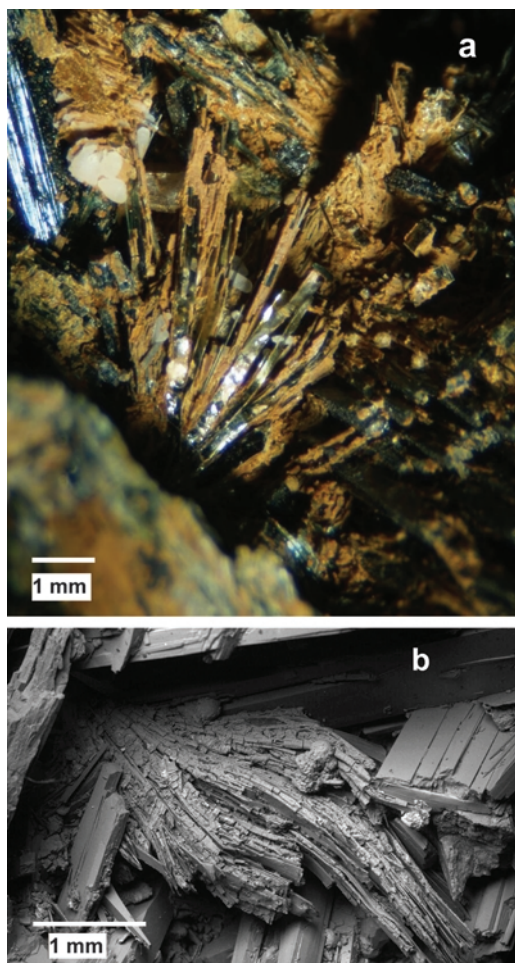


FIG. 1. Sveinbergeite from Buer, Vesterøya, Sandefjord (from Svein A. Berge's collection): (a) rosette-like aggregates of lamellar crystals; photo by Frode Andersen; (b) an aggregate of bent crystals; SEM image by Harald Folvik.

TABLE 1. Comparison of the properties of sveinbergeite and astrophyllite*.

	Sveinbergeite	Astrophyllite
Formula	$\text{Ca}(\text{Fe}_6^{2+}\text{Fe}^{3+})\text{Ti}_2(\text{Si}_4\text{O}_{12})_2\text{O}_2(\text{OH})_5(\text{H}_2\text{O})_4$	$\text{K}_2\text{NaFe}_7^{2+}\text{Ti}_2(\text{Si}_4\text{O}_{12})_2\text{O}_2(\text{OH})_4\text{F}$
System	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	5.329 (4)	5.36–5.42
b	11.803(8)	11.85–11.95
c	11.822 (8)	11.66–11.75
α (°)	101.140 (8)	112.03–113.13
β	98.224 (8)	94.52–94.64
γ	102.442 (8)	103.08–103.14
V (Å ³)	699.0(8)	652.9–668.5
Z	1	1
$D_{\text{meas}}/D_{\text{calc}}$ (g/cm ³)	n.d./3.152	3.09–3.23/3.35
	11.395(100)	10.6 (100)
	2.880(38)	3.51 (80)
Strongest lines in the powder pattern d_{meas} (Å)	2.640(31)	2.77 (60)
	1.643(24)	2.64 (60)
	2.492(20)	2.57 (60)
	1.616(15)	1.76 (30)
Optical character	Biaxial positive	Biaxial positive
α	1.745	1.678–1.695
β	1.746	1.703–1.726
γ	1.753	1.733–1.758
$\alpha-\gamma$	0.008	0.025–0.063
$2V_{\text{meas}}$ (°)	20	66–84
Optical orientation	$X \perp (001)$ $Y \wedge b = 12^\circ$ $Z = a$	$X \perp (001)$ $Y \wedge b = 13^\circ$ $Z = a$
Colour	Deep green	Bronze-yellow to gold-yellow, brown to reddish brown
Pleochroism	$X =$ brownish green $Y =$ brownish green $Z =$ deep green	$X =$ deep orange-red $Y =$ orange-yellow $Z =$ lemon-yellow

* Data for astrophyllite are taken from Anthony *et al.* (1995: p.46, 355) except those for cell parameters (from Piilonen *et al.*, 2003b) and optical orientation (from Nickel *et al.*, 1964).

fluoresce when exposed to 240–400 nm ultra-violet radiation. The crystals are flexible and are commonly bent. They have a perfect to micaceous {001} cleavage, uneven fracture and a Mohs hardness of 3. The density of sveinbergeite could not be measured accurately because of the very small thickness of the crystals. Its calculated density (using the empirical formula) is 3.152 g/cm³. The mineral is biaxial positive with α 1.745(2), β 1.746(2), γ 1.753(2) ($\lambda = 589$ nm), $2V(\text{meas.}) = 20(3)^\circ$, $2V(\text{calc.}) = 41.5^\circ$,

with no discernible dispersion. It is pleochroic according to the scheme $Z > X \sim Y$ (medium) where Z is deep green, X and Y are brownish green. Orientation is as follows: $X \perp (001)$, $Y \wedge b = 12^\circ$, $Z = a$, elongation positive. A Gladstone-Dale calculation gives a compatibility index of -0.002 (calculated using a molar refraction for Fe_2O_3 of 0.268), which is rated as superior (Mandarino, 1981). Note that the calculated value of $2V$ (41.5°) is considerably different from the value measured using a universal stage:

20(3)°. However, the value of $2V$ is dependent on the differences between the principal refractive indices and when these are very close, the differences in the refractive indices are not very accurate; the difference between the measured values of α and β , 0.001(2)°, results in an imprecise calculated value of $2V$.

The infrared spectrum of sveinbergeite (Fig. 2) contains the following set of absorption frequencies (cm^{-1}): 3588 (OH-stretch), ~3398 (broad) + ~3204 (broad) (both H_2O stretches), 1628 (H–O–H bend), 1069, 1009, 942 (Si–O stretches), 702, 655 (Si–O–Si bend), 560 (Si–O–Ti). Therefore, the spectrum confirms the presence of H_2O and OH groups in the mineral structure.

When heated at 500°C, sveinbergeite crystals became isotropic and their colour changed from deep green to bright orange. Physical and optical properties of crystals heated at 150°C are identical to those before heating. The mineral is not affected by cold 1:1 water solutions of HCl or HNO_3 .

Chemical composition

Mössbauer spectroscopy

Transmission Mössbauer spectroscopy measurements on sveinbergeite were made at room temperature (RT) using a $^{57}\text{Co}(\text{Rh})$ point source. A metallic Fe foil was used for the calibration of the spectrometer and spectra were collected in the velocity range of ± 4 mm/s. We first collected a Mössbauer spectrum on a powdered sample of

oxide-coated sveinbergeite. The spectrum was fitted with two sites, one for Fe^{2+} and the other for Fe^{3+} (each having two overlapping Gaussian components), using a Voigt-based quadrupole-splitting distribution method implemented in the *Recoil* software suite. From the Mössbauer relative areas, we obtained a $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio of 0.60(1), which is significantly larger than the value calculated from the structure refinement (0.16), indicating that the coating was contributing to the Fe^{3+} component of the spectrum. We cleaned the sveinbergeite crystals (not completely as it was not possible) and collected a Mössbauer spectrum on a few cleaner single crystals; this is shown in Fig. 3. It indicates that 67% of Fe is present as Fe^{2+} , 25% as Fe^{3+} and 8% as Fe^{3+} impurity. Normalization of Fe^{2+} and Fe^{3+} values for sveinbergeite gives a $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio of 25(10)%, which is in better agreement with the 16% calculated from the structure refinement.

Electron-microprobe analysis

The chemical composition of sveinbergeite (Table 2) was determined using a Cameca SX-100 electron microprobe operating in wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, a beam size of 10 μm and count times on peak and background of 2 s and 10 s, respectively. We used the following standards: $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ (Nb), titanite (Ti), zircon (Zr), diopside (Si, Ca), andalusite (Al), fayalite (Fe), spessartine (Mn), forsterite (Mg), orthoclase (K), albite (Na) and

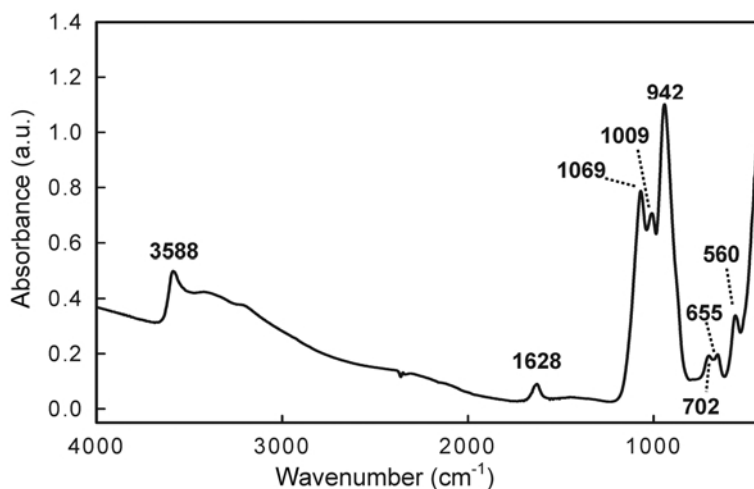


FIG. 2. The IR spectrum of sveinbergeite.

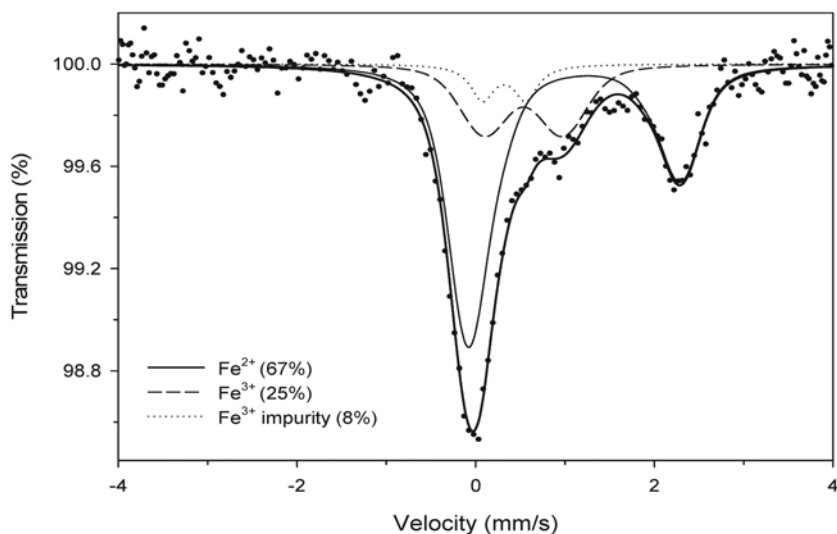


FIG. 3. Mössbauer spectrum of sveinbergeite collected at room temperature. The spectrum is fitted with three sites, Fe²⁺ (solid-line subspectrum, 67% relative area), Fe³⁺ (dashed-line subspectrum, 25% relative area), and Fe³⁺ impurity (dotted-line subspectrum, 8% relative area) using a Voigt-based quadrupole-splitting distribution method.

F-bearing riebeckite (F). The elements Sr, Sn, Cs, Zn, Ba, Ta, Pb and Rb were sought but not detected. The H₂O content was not determined

directly because insufficient material was available; it was calculated by stoichiometry from the crystal-structure analysis and its presence was

TABLE 2. Chemical composition and unit formula* of sveinbergeite.

Oxide	Wt.%	Range	Cation	a.p.f.u.
Nb ₂ O ₅	0.55	0.41–0.84	Nb	0.06
TiO ₂	10.76	10.24–11.28	Ti	1.86
ZrO ₂	0.48	0.13–1.35	Zr	0.05
SiO ₂	34.41	33.00–35.41	Si	7.91
Al ₂ O ₃	0.34	0.00–0.69	Al	0.09
Fe ₂ O ₃ **	5.57		Fe ³⁺	0.96
FeO **	29.39 (34.40 _{tot})	(33.86–34.92 _{tot})	Fe ²⁺	5.65
MnO	1.27	0.71–1.74	Mn	0.25
CaO	3.87	3.10–4.09	Ca	0.95
MgO	0.52	0.41–0.67	Mg	0.18
K ₂ O	0.49	0.11–1.53	K	0.14
Na ₂ O	0.27	0.10–0.77	Na	0.12
F	0.24	0.03–0.63	Σ cations	18.22
H ₂ O***	8.05		F	0.17
O=F	–0.10		Σ anions	34.78
Total	96.11		H	12.34

* calculated on 8(Si + Al) a.p.f.u.;

** calculated from structure solution and refinement in accord with determination by Mössbauer spectroscopy as outlined in the text;

*** calculated from structure solution and refinement.

confirmed by infrared spectroscopy. On the basis of eight (Si + Al) per formula unit ($Z = 1$), the following empirical formula was obtained for sveinbergeite: $(\text{Ca}_{0.95}\text{Na}_{0.12}\text{K}_{0.14})_{\Sigma 1.21}(\text{Fe}_{5.65}^{2+}\text{Fe}_{0.93}^{3+}\text{Mn}_{0.25}\text{Mg}_{0.18})_{\Sigma 7.01}(\text{Ti}_{1.86}\text{Nb}_{0.06}\text{Zr}_{0.05}\text{Fe}_{0.03}^{3+})_{\Sigma 2}(\text{Si}_{7.91}\text{Al}_{0.09})_{\Sigma 8}\text{O}_{34.61}\text{H}_{12.34}\text{F}_{0.17}$ (see section 'Chemical formula' below). The simplified formula is $\text{Ca}(\text{Fe}_6^{2+}\text{Fe}^{3+})\text{Ti}_2(\text{Si}_4\text{O}_{12})_2\text{O}_2(\text{OH})_5(\text{H}_2\text{O})_4$, which requires CaO 4.23, FeO 32.54, Fe_2O_3 6.03, SiO_2 36.29, TiO_2 12.06, H_2O 8.84, total 100.00 wt.%.

X-ray powder diffraction

The powder-diffraction pattern for sveinbergeite was recorded using a Bruker D8 Discover SuperSpeed micro-powder diffractometer with a multi-wire 2D detector and a modified Gandolfi attachment. Table 3 shows the X-ray powder-diffraction data (for $\text{Cu-K}\alpha$, $\lambda = 1.54178 \text{ \AA}$; 50 kV/60 mA, two 10-h frames merged, no internal standard used) together with the refined unit cell dimensions; the latter are in close agreement with corresponding values determined by single-crystal diffraction (Table 1).

Crystal structure

X-ray data collection and structure refinement

Many crystals were examined on a Bruker AXS SMART APEX diffractometer. In some cases, the diffraction patterns were of low quality and could not be indexed satisfactorily. Five grains produced diffraction patterns which could be indexed and intensity data were collected on all five crystals according to the following methodology (where specific information relates to the refinement with the lowest R_1 index). X-ray diffraction data for crystal #3 were collected using a Bruker AXS SMART APEX diffractometer with a CCD detector ($\text{Mo-K}\alpha$ radiation). The intensities of 5329 reflections with $-6 < h < 6$, $-14 < k < 14$, $-14 < l < 14$ were collected to $51^\circ 2\theta$ using a 1° frame and an integration time of 60 s. The refined unit-cell parameters were obtained from 1231 reflections with $I > 10\sigma I$ (Tables 1 and 4), and an empirical absorption correction (*SADABS*, Sheldrick, 2008) was applied. The crystal structure of sveinbergeite was solved by direct methods and refined to an R_1 value of 21.81% using the Bruker *SHELXTL* version 5.1 system of programs (Sheldrick, 2008). The crystals of sveinbergeite are of very poor diffraction quality, and we were fortunate to find a single crystal with a diffraction

TABLE 3. X-ray powder diffraction data for sveinbergeite.

I_{obs}	$d_{\text{obs}} (\text{\AA})$	$d_{\text{calc}} (\text{\AA})$	$h k l$
100	11.395	11.502	0 0 1
		11.314	0 1 0
28 S	10.403*		
10	5.698	5.751	0 0 2
6	5.069	5.035	$\bar{1}$ 0 1
7	4.791	4.759	0 1 2
10	4.348	4.346	$\bar{1}$ 2 0
		4.300	1 1 0
8	3.810	3.834	0 0 3
5	3.702	3.684	0 2 2
38	2.880	2.875	0 0 4
12	2.757	2.770	$\bar{1}$ 4 0
		2.747	$\bar{1}$ $\bar{3}$ 2
31	2.640	2.638	$\bar{2}$ 1 0
		2.636	$\bar{1}$ 4 1
20	2.492	2.495	2 $\bar{1}$ 1
3	2.406	2.407	$\bar{1}$ 4 2
13	2.270	2.279	$\bar{1}$ $\bar{3}$ 4
		2.278	2 $\bar{1}$ 2
10	2.194	2.196	2 0 2
7	2.104	2.098	1 $\bar{4}$ 4
5	2.019	2.019	$\bar{1}$ $\bar{3}$ 5
11	1.806	1.806	$\bar{2}$ $\bar{3}$ 4
10	1.788	1.787	$\bar{1}$ $\bar{3}$ 6
24	1.643	1.646	0 $\bar{7}$ 1
		1.643	0 $\bar{7}$ 2
15	1.616	1.616	0 7 0
14	1.573	1.573	$\bar{3}$ $\bar{2}$ 2
9	1.552	1.552	$\bar{3}$ 5 0

Indexing based on the refined unit-cell parameters:

$a = 5.330(6)$, $b = 11.803(12)$, $c = 11.855(16) \text{ \AA}$;

$\alpha = 99.34(15)$, $\beta = 98.182(15)$, $\gamma = 102.05(11)^\circ$;

$V = 707.6(1.2) \text{ \AA}^3$.

S = shoulder;

* not used for refinement.

pattern which we were able to index. Although the resulting R_1 index (Table 4) is very high, there is no doubt of the correctness of the structure topology as all five structure refinements produced the same structural connectivity. Some of the interatomic distances obtained from the refined structure were not realistic, specifically some Si–O distances, and we constrained these to more realistic values to obtain better interatomic distances at adjacent sites. For sveinbergeite, we observed a split of the *B* site into two sites, *B*(1) and *B*(2), ~50% occupied by Ca and H_2O , respectively, and separated by a short distance

TABLE 4. Miscellaneous refinement data for sveinbergeite.

a (Å)	5.329 (4)
b	11.803(8)
c	11.822 (8)
α (°)	101.140 (8)
β	98.224 (8)
γ	102.442 (8)
V (Å ³)	699.0(8)
Space group	$P\bar{1}$
Z	1
Absorption coefficient (mm ⁻¹)	4.66
$F(000)$	651.3
$D_{\text{calc.}}$ (g/cm ³)	3.152
Crystal size (mm)	0.275 × 0.150 × 0.010
Radiation/filter	Mo-K α /graphite
2 θ -max for structure refinement (°)	51.00
$R(\text{int})$ (%)	6.47
Reflections collected	5324
Independent reflections	2432
$F_o > 4\sigma F$	2177
Refinement method	Full-matrix least squares on F^2 , fixed weights proportional to $1/\sigma F_o^2$
No. of refined parameters	171
Final R (obs) (%)	
$[F_o > 4\sigma F]$	21.81
R_1	22.95
wR_2	43.97
Goodness of fit on F^2	1.239

(0.95 Å). We examined the possibility of Ca–H₂O order by refining the structure in a lower symmetry. Refinement in space group $P1$ converged to $R_1 \sim 16\%$, but the structure showed Ca–H₂O disorder as in the space group $P\bar{1}$, i.e. splitting of the B site. Hence, we chose a higher symmetry, space group $P\bar{1}$, to characterize the structure of sveinbergeite. Site-scattering values were refined for the D site with the scattering curve of Ti, M sites (scattering curve of Fe), B site (scattering curves of Ca and O) and A site (scattering curve of O). For the $M(1)$ and $M(4)$ sites, refinement converged to integer values and hence they were fixed at full occupancies. At the last stage of the refinement, site occupancies were fixed for the D , $B(1)$ and $B(2)$ sites, and most Si–O bond lengths were fixed at reasonable values. Scattering curves for neutral atoms were taken from *International Tables for Crystallography* (Wilson, 1992). Details of the data collection and structure refinement are given in Table 4, final atom parameters are given in Table 5, selected interatomic distances in Table 6,

refined site-scattering values and assigned populations for selected cation sites are given in Table 7 and bond-valence values in Table 8. A table of structure factors has been deposited with the Principal Editor of *Mineralogical Magazine* and is available from www.minersoc.org/pages/e_journals/dep_mat.html.

Topology of the structure

In the sveinbergeite structure, the main structural unit is an HOH layer (Fig. 4a) which is topologically identical to that in astrophyllite, K₂NaFe²⁺Ti₂(Si₄O₁₂)₂O₂(OH)₄F (Piilonen *et al.*, 2003b) (Fig. 4b). The $M(1)$, $M(2)$, $M(3)$ and $M(4)$ octahedra (C-group) share edges to form an O sheet of close-packed octahedra. The characteristic feature of the astrophyllite structure is an (Si₄O₁₂) ribbon that extends along [100]. The (Si₄O₁₂) astrophyllite ribbons share common vertices with D octahedra to form the heteropolyhedral (H) sheet. In the crystal structures of the astrophyllite-group minerals, the O sheet and

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TABLE 5. Atom coordinates and isotropic displacement parameters (\AA^2) for sveinbergeite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*
M(1)**	0.8452(9)	0.7086(4)	0.9777(4)	0.0079(12)
M(2)**	0.2825(10)	0.5692(4)	0.9894(5)	0.0097(19)
M(3)**	0.5788(9)	0.1474(4)	0.0179(4)	0.0047(18)
M(4)**	0	0	0	0.0059(15)
D**	0.4002(11)	0.6517(5)	0.7186(6)	0.0102(14)
T(1)	0.1514(18)	0.1039(8)	0.7805(9)	0.017(2)
T(2)	0.7096(17)	0.2282(8)	0.7805(9)	0.017(2)
T(3)	0.8419(18)	0.4900(8)	0.7578(8)	0.009(2)
T(4)	0.989(2)	0.8295(8)	0.7533(9)	0.019(2)
A**	0.444(8)	0.854(4)	0.521(4)	0.088(16)
B(1)**	0.188(5)	0.391(2)	0.485(2)	0.050(6)
B(2)**	0.201(17)	0.339(8)	0.537(8)	0.050(6)
O(1)	0.054(5)	0.9602(9)	0.7182(17)	0.019(6)
O(2)	0.729(5)	0.3456(10)	0.7250(19)	0.027(7)
O(3)	0.678(6)	0.777(3)	0.703(3)	0.034(7)
O(4)	0.100(6)	0.521(4)	0.704(4)	0.068(12)
O(5)	0.905(5)	0.538(2)	0.900(2)	0.018(5)
O(6)	0.627(7)	0.550(3)	0.694(3)	0.045(9)
O(7)	0.092(4)	0.847(2)	0.2746(16)	0.022(6)
O(8)	0.771(5)	0.264(2)	0.9250(11)	0.015(5)
O(9)	0.211(5)	0.133(2)	0.9199(11)	0.013(5)
O(10)	0.948(4)	0.1604(18)	0.1103(11)	0.005(4)
O(11)	0.154(6)	0.751(3)	0.689(3)	0.032(7)
O(12)	0.592(3)	0.849(2)	0.2742(16)	0.022(6)
O(13)	0.465(6)	0.691(3)	0.879(2)	0.027(6)
O(14)**	0.337(4)	0.399(2)	0.9150(19)	0.009(5)
O(15)**	0.376(5)	0.012(2)	0.0901(19)	0.011(5)
X**	0.315(6)	0.611(3)	0.540(3)	0.034(7)
Subsidiary peaks				
1	$\frac{1}{2}$	0	0	0.01
2	0.63(4)	0.294(16)	0.957(16)	0.01
3	0.267(14)	0.419(6)	0.986(6)	0.01
4	0.281(18)	0.798(8)	0.719(8)	0.01

* U_{eq} for D, M(1–4) and T(1–4) atoms

** see Table 7 for assigned site-populations

two H sheets form an HOH layer of composition $\text{C}_7\text{D}_2(\text{Si}_4\text{O}_{12})_2\text{O}_2(\text{OH})_4\text{X}_{0-1}$. Along [001], these HOH blocks connect via common X anions of the D octahedra and interstitial cations at the A and B sites (Fig. 4b). In sveinbergeite, the linkage of HOH layers and the chemical composition of the interstitial sites are different from any other mineral of the astrophyllite group. In the sveinbergeite structure, D octahedra do not share a common vertex (X site) as in astrophyllite; the HOH layers link via Ca atoms and hydrogen bonds involving H_2O groups (Fig. 4a).

Cation sites

Site populations were assigned on the basis of the refined site-scattering values (Table 7), the chemical formulae (Table 2) derived from electron-microprobe analysis and the Mössbauer results, and the observed mean bond lengths (Table 6).

There are ten cation sites in the crystal structure of sveinbergeite. In the HOH layer [as in astrophyllite, Piilonen *et al.* (2003b)], there are nine cation sites; site labelling is in accord with Piilonen *et al.* (2003b).

TABLE 6. Selected interatomic distances (Å) and angles (°) for sveinbergeite.

M(1)–O(9)e	2.12(2)	M(2)–O(5)i	2.06(3)	M(3)–O(10)l	2.07(2)
M(1)–O(8)f	2.12(2)	M(2)–O(14)e	2.09(2)	M(3)–O(9)l	2.09(2)
M(1)–O(13)	2.13(3)	M(2)–O(14)	2.13(2)	M(3)–O(8)	2.11(2)
M(1)–O(14)e	2.15(2)	M(2)–O(8)e	2.13(2)	M(3)–O(15)	2.12(2)
M(1)–O(5)	2.16(2)	M(2)–O(5)e	2.19(3)	M(3)–O(13)a	2.13(3)
M(1)–O(10)g	<u>2.21(2)</u>	M(2)–O(13)	<u>2.28(3)</u>	M(3)–O(15)c	<u>2.14(2)</u>
<M(1)–O>	<u>2.15</u>	<M(2)–O>	<u>2.15</u>	<M(3)–O>	<u>2.11</u>
M(4)–O(15)	2.09(2) × 2	D–O(13)	1.83(3)	T(1)–O(9)	1.59(1)
M(4)–O(10)c	2.18(2) × 2	D–O(6)	1.90(4)	T(1)–O(12)a	1.63(1)
M(4)–O(9)l	<u>2.18(2) × 2</u>	D–O(3)	1.91(3)	T(1)–O(7)b	1.63(1)
<M(4)–O>	<u>2.15</u>	D–O(4)	1.93(3)	T(1)–O(1)j	<u>1.65(1)</u>
		D–O(11)	1.97(2)	<T(1)–O>	1.63
		D–X	<u>2.03(3)</u>		
		<D–O>	1.93		
T(2)–O(2)	1.63(1)	T(3)–O(4)d	1.60(1)	T(4)–O(10)g	1.58(1)
T(2)–O(12)a	1.64(1)	T(3)–O(5)	1.62(3)	T(4)–O(11)d	1.58(1)
T(2)–O(8)	1.65(1)	T(3)–O(2)	1.63(1)	T(4)–O(3)	1.61(3)
T(2)–O(7)a	<u>1.65(1)</u>	T(3)–O(6)	<u>1.64(4)</u>	T(4)–O(1)d	<u>1.65(1)</u>
<T(2)–O>	<u>1.64</u>	<T(3)–O>	<u>1.62</u>	<T(4)–O>	<u>1.61</u>
T(1)b–O(7)–T(2)a	135(1)	T(1)h–O(1)–T(4)i	140(1)		
T(1)a–O(12)–T(2)a	135(1)	T(2)–O(2)–T(3)	143(1)	<T–O–T>	138
A*–O(3)	2.74(5)	B(1)–X	2.47(4)	B(1)–B(2)	0.95(9)
A–X	2.87(5)	B(1)–O(11)b	2.58(4)	A–B(2)a	3.3(1)
A–O(11)	2.97(5)	B(1)–O(6)a	2.61(4)	A–Ak	3.51(9)
A–O(12)	3.12(5)	B(1)–Xb	2.65(4)		
A–O(7)	3.20(4)	B(1)–Xa	2.71(4)		
A–O(2)a	3.24(5)	B(1)–O(4)	2.90(5)		
A–O(1)d	3.54(5)	B(1)–O(3)a	2.95(4)		
A–O(1)	<u>3.56(5)</u>	B(1)–O(4)b	3.01(5)		
<A–O>	<u>3.16</u>	B(1)–O(6)	<u>3.12(4)</u>		
		<B(1)–O>	<u>2.78</u>		

a = –y+1, –y+1, –z+1; b = –y, –y+1, –z+1; c = –y+1, –y, –z; d = y+1, y, z; e = –y+1, –y+1, –z+2;

f = –y+2, –y+1, –z+2; g = –y+2, –y+1, –z+1; h = y, y+1, z; i = y–1, y, z; j = y, y–1, z; k = –y+1, –y+2, –z+1;

l = y, y, z–1.

* A = K.

H sheet

There are five cation sites in the H sheet. The *D* site is occupied by $\text{Ti}_{1.86}\text{Nb}_{0.06}\text{Zr}_{0.05}\text{Fe}_{0.03}^{3+}$ a.p.f.u., and is coordinated by five O atoms and an X anion where X = H₂O, OH, F; <D–φ> = 1.93 Å (φ = unspecified anion). The ideal composition of the *D* site is Ti₂ a.p.f.u. The four *T* sites are occupied mainly by Si with minor Al, Si_{7.91}Al_{0.09} p.f.u. Mean T–O distances vary from 1.61 to 1.64 Å and T–O–T angles vary from 135° to 143° (Table 6).

M sites of the C-group in the O sheet

In sveinbergeite, the sum of the medium-sized divalent (Fe²⁺, Mn²⁺, Mg²⁺) and trivalent (Fe³⁺) cations is 7.01 a.p.f.u. (Table 2; 0.03 Fe³⁺ a.p.f.u. has been allocated to the *D* site, see above), indicating that the *M*(1–4) sites are fully occupied by Fe²⁺, Mn²⁺, Mg²⁺ and Fe³⁺, with a total calculated scattering of 179.4 e.p.f.u. (electrons per formula unit). This observation is in accord with the total refined site-scattering of 175 e.p.f.u. for the *M*(1–4) sites (Table 7). In astrophyllite-

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TABLE 7. Refined site-scattering and assigned site-populations for sveinbergeite.

Site*	Refined site-scattering (e.p.f.u.)	Assigned site-population (a.p.f.u.)	Calculated site-scattering (e.p.f.u.)	$\langle X-\varphi \rangle_{\text{obs.}}$ (Å)
M(1)	52			2.15
M(2)	48(1)			2.15
M(3)	49(1)			2.11
M(4)	26			2.15
Total M(1–4)	175	5.65 Fe ²⁺ + 0.93 Fe ³⁺ + 0.25 Mn + 0.17 Mg	179.4	
D	46	1.86 Ti + 0.06 Nb + 0.05 Zr + 0.03 Fe ³⁺	46.2	1.93
[⁸]A**	16(2)	1.86 H ₂ O + 0.14 K	17.5	3.16**
[⁹]B(1)	20.4	0.95 Ca + 0.12 Na + 0.93 □	20.3	2.78
B(2)	7.4	0.93 H ₂ O + 1.07 □	7.4	
X	16	0.93 H ₂ O + 0.90 OH + 0.17 F	16.2	
O(14)	16	2.00 OH		
O(15)	16	2.00 OH		

* coordination number is shown for a non-octahedral site; φ represents an unspecified anion;

** the A site is [8]-coordinated by O atoms with $\langle A-O \rangle = 3.16$ Å where it is occupied by K.

TABLE 8. Bond valence (v.u.) for sveinbergeite*.

Atom	T(1)	T(2)	T(3)	T(4)	D	M(1)	M(2)	M(3)	M(4)	B(1)	Σ
O(1)	0.95			0.95							1.90
O(2)		1.00	1.00								2.00
O(3)				1.05 ^{×2} ↓	0.75 ^{×2} ↓					0.05	1.86
O(4)			1.08		0.71					0.06	1.90
O(5)							0.43	0.33		0.05	2.09
O(6)			0.98		0.77		0.30			0.10	1.89
[³]O(7)	1.00	0.95								0.04	1.95
O(8)		0.95				0.38	0.35	0.36			2.04
O(9)	1.11					0.40		0.36	0.31 ^{×2} ↓		2.18
O(10)				1.14		0.42		0.29	0.31 ^{×2} ↓		2.16
O(11)				1.14	0.64					0.10	1.90
O(12)	1.00	0.98									1.98
O(13)					0.93	0.35	0.24	0.35			1.87
[³]O(14)							0.39	0.34			1.08
[³]O(15)						0.37	0.35		0.39 ^{×2} ↓		1.11
X					0.54					0.13	0.84
										0.09	
										0.08	
Total	4.06	3.88	4.09	4.28	4.37	2.23	2.06	2.03	2.02	0.70	
Aggregate charge	3.99	3.99	3.99	3.99	4.02		Total M(1–4): 8.50			1.01	

* calculated with bond-valence parameters of Brown (1981);

coordination number is shown for non-[4]-coordinated anions; O(14) = O(15) = OH;

X = $\frac{1}{2} \times [(H_2O)_{0.93}(OH)_{0.90}F_{0.17}]$.

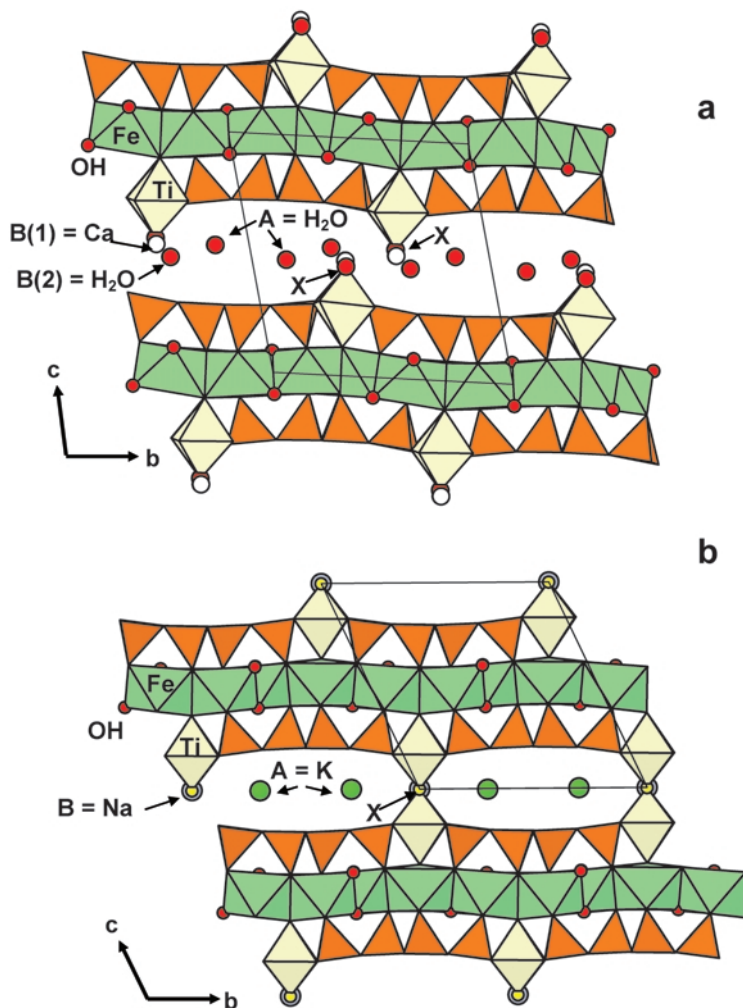


FIG. 4. General view of the crystal structures of (a) sveinbergeite and (b) astrophyllite. The Fe-dominant and Ti octahedra are green and yellow, respectively; Si tetrahedra are orange, Ca, Na and K atoms are shown as white, blue and green spheres, H₂O groups and OH groups and F atoms are shown as large red and smaller red and yellow spheres, respectively.

group minerals, the size of the M polyhedra follows the pattern $M(1) > M(2) > M(3) > M(4)$ (Piilonen *et al.*, 2003b). In sveinbergeite, $\langle M-\phi \rangle$ distances vary from 2.15 Å [M(1,2,4)] to 2.11 Å [M(3)], the differences being within their estimated standard deviations (Table 6). The similarity of individual mean bond lengths and of refined site-scattering values do not allow derivation of individual site populations for the M(1–4) sites. We can only state that Fe²⁺ is the dominant cation at all four M sites (Table 7). The M(1–4) sites give Fe_{5.65}Fe_{0.93}Mn_{0.25}Mg_{0.17} a.p.f.u. (total

charge 14.93⁺) which is in good agreement with the ideal composition of Fe₆²⁺Fe³⁺ a.p.f.u. (charge 15⁺).

The A and B interstitial sites

In the structure of astrophyllite, there are two interstitial sites, the K-dominant A site and the Na-dominant B site (Fig. 4b). In sveinbergeite, the A site is occupied mainly by H₂O and minor K (Table 7). A short A–A distance of 3.51 Å (Table 6) indicates that the A site cannot be fully occupied by K. Where the A site is 7% occupied

by K, the K atom is coordinated by seven O atoms and an X anion, with $\langle K-\varphi \rangle = 3.16 \text{ \AA}$ (Table 6). Where the *A* site is 93% occupied by H₂O, that H₂O group is connected via hydrogen bonding to another symmetrically equivalent H₂O group, an X anion and O(3) and O(11) atoms. The latter two atoms are at distances of 2.74 and 2.97 Å from the *A* site, respectively, and receive bond valence of 1.86 and 1.90 v.u. (valence units) (Table 8). Therefore they can be considered as potential acceptors of hydrogen bonds. The *A* site is occupied by (1.86 H₂O + 0.14 K) p.f.u., or ideally (H₂O)₂ p.f.u.

The *B* site of astrophyllite (Fig. 4*b*) is split into two sites in sveinbergeite, *B*(1) and *B*(2). The *B*(1) and *B*(2) sites are separated by 0.95 Å, and hence cannot both be occupied at the local scale [i.e. occupancy of one site precludes occupancy of the locally adjacent site]. In accord with the refined site scattering, we assigned (0.95 Ca + 0.12 Na + 0.93 □) p.f.u. to the *B*(1) site (refined site scattering of 20.4 e.p.f.u.) and (0.93 H₂O + 1.07 □) p.f.u. to the *B*(2) site (refined site scattering of 7.4 e.p.f.u.) (Table 7). The *B*(1) site is coordinated by six O atoms and three X anions, with a $\langle B(1)-\varphi \rangle$ distance of 2.78 Å where $\varphi = O, H_2O, OH, F$. The ideal compositions of the *B*(1) and *B*(2) sites are (Ca□) and [(H₂O)□] p.f.u. and the ideal composition of the *B* site is [Ca(H₂O)] p.f.u. The details of the split of the *A* site into two and three sites have been summarized for the astrophyllite-group minerals by Cámara *et al.* (2010). However, sveinbergeite is the first mineral of the astrophyllite group, for which a splitting of the *B* site has been recorded.

We write an ideal A₂B₂C₇D₂ component of the structure for sveinbergeite as follows (H₂O)₂ [Ca(H₂O)] Fe₆²⁺Fe₃³⁺Ti₂ (cf. the A₂BC₇D₂ component for astrophyllite).

Anion considerations

In sveinbergeite, there are sixteen sites that are fully occupied by anions, O(1–15) and X; the two *A* and *B*(2) sites are occupied by (1.86 H₂O + 0.14 K) p.f.u. and (0.93 H₂O + 1.07 □) p.f.u., respectively (see above). The O(1–12) belong to (SiO₄) tetrahedra and give 24 O atoms p.f.u. which correspond to two astrophyllite (Si₄O₁₂) ribbons. There is one site, O(13), which receives bond valence from three M atoms and a D atom, giving O₂ p.f.u. There are two sites, O(14) and O(15), which receive bond valence from three M atoms and are occupied by OH groups. Bond

valence incident at each of these two sites sums to 1.08 and 1.11 v.u., respectively (Table 8). The two O(14) and O(15) sites give (OH)₄ p.f.u.

Short-range order at the X site

Due to cation disorder at the *B* site [which is split into *B*(1) and *B*(2) sites, see above], there is anion disorder at the *X* site. Figure 5 illustrates short range order around the *X* site. The *X* site is occupied by OH groups where it receives bond valence from the Ti atom at the *D* site and Ca atoms at three *B*(1) sites, and is connected to an H₂O group at the *A* site via hydrogen bonding (Fig. 5*a*). The *X* site is occupied by H₂O groups where it receives bond valence from the Ti atom at the *D* site, and is connected to H₂O groups at three *B*(2) sites and an H₂O group at the *A* site (Fig. 5*b*). Taking into account the chemical composition of the *B*(1) and *B*(2) sites, (Ca_{0.95}Na_{0.12}□_{0.93}) and [(H₂O)_{0.93}□_{1.07}], we write the composition of the *X* site as [(H₂O)_{0.93}(OH)_{0.90}F_{0.17}], ideally [(OH)(H₂O)] p.f.u. Note that the arrangement of hydrogen bonds in Fig. 5*b* is very similar to that described for murmanite, Na₄Ti₄(Si₂O₇)₂O₄(H₂O)₄ (Cámara *et al.*, 2008) and proposed for epistolite, Na₄TiNb₂(Si₂O₇)₂O₂(OH)₂(H₂O)₄ (Sokolova and Hawthorne, 2004).

For sveinbergeite, we write the anion part of the structure as (Si₄O₁₂)₂O₂(OH)₄[(OH)(H₂O)].

Chemical formula

Piilonen *et al.* (2003*a*) wrote the general formula for astrophyllite-group minerals as A₂BC₇D₂T₈O₂₆(OH)₄X_{0–1}. Cámara *et al.* (2010) suggested writing the general formula of the astrophyllite-group minerals as A₂BC₇D₂(T₄O₁₂)₂O₂(OH)₄X_{0–1} as this preserves the correct formula for the (T₄O₁₂) astrophyllite silicate ribbon, and identifies the O₂ anion component of the structure as not bonded to Si. In this paper, we adjust a general formula of Cámara *et al.* (2010) to take account of sveinbergeite. Site occupancies for the HOH layer and interstitial sites provide the information summarized in Table 9.

We can write the ideal structural formula of sveinbergeite as A₂B₂C₇D₂(T₄O₁₂)₂O₂(OH)₄X₂: (H₂O)₂[Ca(H₂O)](Fe₆²⁺Fe₃³⁺)(Si₄O₁₂)₂O₂(OH)₄ [(OH)(H₂O)], which agrees with the detailed empirical formula, [(H₂O)_{1.86}K_{0.14}]_{Σ2} {(Ca_{0.95}Na_{0.12}□_{0.93})[(H₂O)_{0.93}□_{1.07}]}_{Σ4} (Fe_{3.65}²⁺Fe_{0.93}³⁺Mn_{0.25}Mg_{0.18})_{Σ7.01}(Ti_{1.86}Nb_{0.06}Zr_{0.05}Fe_{0.03}³⁺)_{Σ2}(Si_{7.91}Al_{1.09}O_{9.24})O₂(OH)₄

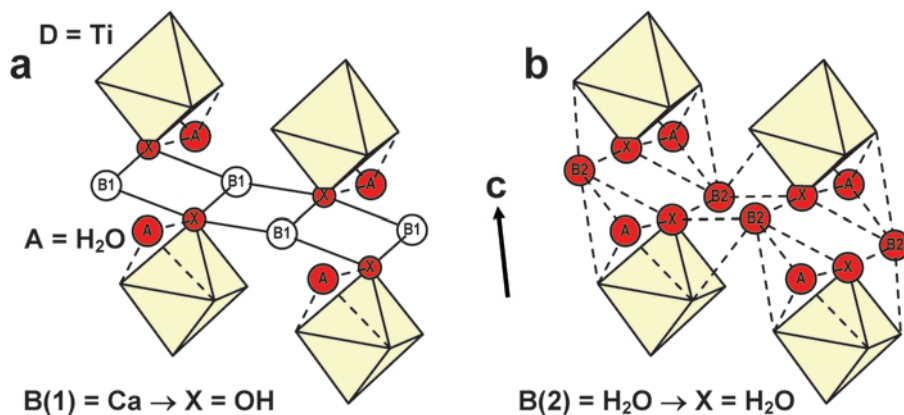


FIG. 5. Short range order (SRO) arrangements around the X site in the crystal structure of sveinbergeite: (a) the X site is occupied by an OH group where it receives bond valence from the Ti atom at the D site and three Ca atoms at the $B(1)$ sites, and there is a hydrogen bond to an H_2O group at the A site; (b) the X site is occupied by an H_2O group where it receives bond valence from the Ti atom at the D site, and there are bonds to three H_2O groups at the $B(2)$ sites and an H_2O group at the A site. The Ca atoms at the $B(1)$ sites are shown as white spheres, Ti octahedra are yellow, H_2O and OH groups are shown as large and medium red spheres, Ca– X bonds are shown as solid black lines, possible directions of hydrogen bonds are shown by dashed lines between two O atoms.

$[(H_2O)_{0.93}(OH)_{0.90}F_{0.17}]_{\Sigma 2}$, $Z = 1$. The simplified formula of sveinbergeite is $Ca(Fe_6^{2+}Fe^{3+})Ti_2(Si_4O_{12})_2O_2(OH)_5(H_2O)_4$, $Z = 1$.

Relation to astrophyllite

Sveinbergeite is a new mineral of the astrophyllite group. The main structural unit in the sveinbergeite structure is an HOH layer that is topologically identical to that in the astrophyllite structure. Sveinbergeite differs from all other minerals of the astrophyllite group in the composition and topology of the interstitial A and B sites and the linkage of adjacent HOH layers. Sveinbergeite and astrophyllite are related by the four binary substitutions at individual sites which are described in Table 10.

To summarize, sveinbergeite and astrophyllite are related by the following substitution: ${}^MFe^{3+} + {}^A(H_2O)_2 + {}^B Ca^{2+} + {}^B(H_2O) + {}^X(H_2O)_2 + {}^X(OH)^- \rightleftharpoons {}^MFe^{2+} + {}^A K^+ + {}^B Na^+ + {}^X F^-$, which clearly indicates the difference in structure type between sveinbergeite and astrophyllite (the four M , X , A and B sites give seven (cation + anions) and five cations per formula unit for sveinbergeite and astrophyllite, respectively). The difference in structure topology reflects the general formulae: $A_2B_2C_7D_2(T_4O_{12})_2O_2(OH)_4X_2$ for sveinbergeite, and $A_2BC_7D_2(T_4O_{12})_2O_2(OH)_4X$ for astrophyllite.

The discovery of sveinbergeite adds a new page to the crystal chemistry of Ti in the astrophyllite group, particularly the self-linkage of the Ti polyhedra. In astrophyllite-group structures, Ti (or Nb) occurs in the H sheet. In sveinbergeite, Ti

TABLE 9. Comparison between the chemical composition of structural elements in sveinbergeite and astrophyllite.

Mineral	— O sheet* —		— 2H sheets —		— Interstitial sites —	
	7 M	6 X^O	2 D (T_4O_{12}) ₂	X_n	2 A	B_n
Sveinbergeite	$Fe_6^{2+}Fe^{3+}$	$O_2(OH)_4$	$Ti_2 (T_4O_{12})_2$	$[(OH)(H_2O)]_{\Sigma 2}$	$(H_2O)_2$	$[{}^{19}Ca(H_2O)]_{\Sigma 2}$
Astrophyllite	Fe_7^+	$O_2(OH)_4$	$Ti_2 (T_4O_{12})_2$	F_1	$[{}^{13}K_2]$	$[{}^{10}Na_1]$

* M = cations of the C group ; X^O = anions in the O sheet not bonded to Si .

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TABLE 10. Substitution mechanisms at different structural sites in sveinbergeite and astrophyllite.

Site	— Sveinbergeite —		Astrophyllite	
		HOH layer		
<i>M</i>	Fe ³⁺	1 a.p.f.u.	⇌	Fe ²⁺ 1 a.p.f.u.
<i>X</i>	(OH) ⁻ (H ₂ O)	2 p.f.u.	⇌	F ⁻ 1 p.f.u.
Interstitial sites				
<i>A</i>	(H ₂ O) ₂	2 p.f.u.	⇌	K ₂ ⁺ 2 a.p.f.u.
<i>B</i>	Ca ²⁺ (H ₂ O)	2 p.f.u.	⇌	Na ⁺ 1 a.p.f.u.
Total		7 p.f.u.	⇌	5 p.f.u.

occurs as isolated {TiO₅X} octahedra where X = H₂O, OH, F (Fig. 4a). In magnesioastrophyllite, Ti is [5]-coordinated and occurs as isolated {TiO₅} polyhedra (Sokolova and Cámara, 2008). In all other astrophyllite-group mineral structures, Ti (or Nb) occurs as a pair of corner sharing {TiO₅X} octahedra which belong to two H sheets of adjacent HOH layers, with X = F, O, OH (Fig. 4b) (Piilonen *et al.*, 2003b, Cámara *et al.*, 2010). Therefore, in the latter structures, the {Ti₂O₁₀X} cluster is characterized by a Ti–X–Ti bridge. The presence of the Ti–X–Ti bridge in the astrophyllite structure makes its crystals brittle; the absence of the Ti–X–Ti bridge in the sveinbergeite structure makes its platy crystals flexible.

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