

Topsøeite, $\text{FeF}_3(\text{H}_2\text{O})_3$, a new fumarolic mineral from the Hekla Volcano, Iceland

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Abstract: The new mineral topsøeite, $\text{FeF}_3(\text{H}_2\text{O})_3$, was found as a fumarolic product after the 1991 eruption of Hekla, Iceland. The mineral occurs as up to 20 μm large square-prismatic crystals forming occasional stepped aggregates or massive, up to 100 μm wide veins, in association with several other fluorides, hematite and opal. The experimental formula of the mineral (from scanning electron microscope energy-dispersive spectrometry data) is $\text{Fe}(\text{F}_{2.94}\text{Cl}_{0.04})_{\Sigma 2.98}(\text{H}_2\text{O})_{1.94}$. The deficiency of water in the formula is most probably an artefact due to experimental limitations and not a sign of dehydration. The mineral is yellow, with a calculated density of $2.330 \text{ g}\cdot\text{cm}^{-3}$, based on the ideal formula. It is tetragonal ($P4/n$) with $a = 7.8381(3) \text{ \AA}$, $c = 3.8674(1) \text{ \AA}$, $V = 237.60(2) \text{ \AA}^3$. The strongest eight powder diffraction lines are [d in Å (relative intensity) (hkl): 5.55 (100) (1 1 0); 3.92 (43) (0 2 0); 3.47 (39) (0 1 1); 3.17 (22) (1 1 1); 2.77 (30) (2 2 0); 2.479 (31) (1 3 0, 3 1 0); 1.877 (16) (0 1 2), 1.753 (24) (2 4 0, 4 2 0). Rietveld refinement of the powder diffraction data confirmed the identity of topsøeite with synthetic $\beta\text{-FeF}_3(\text{H}_2\text{O})_3$. The crystal structure consists of straight infinite chains of $[\text{FeF}_4(\text{H}_2\text{O})_2]$ octahedra extending along the c axis. The adjacent octahedra share apical F atoms, whereas the four unshared, equatorially coordinated atoms are represented by a disordered arrangement of two F and two O atoms from water molecules. Additional water molecules occupy the spaces between chains and are tetrahedrally coordinated by four (F, H_2O) from four different chains binding them together via hydrogen bonds. Topsøeite is isostructural with rosenbergite, $\text{AlF}_3(\text{H}_2\text{O})_3$. Both minerals have rhombohedral polymorphs known from studies of phase systems. The polymorph of topsøeite (UM2008-27-F:AlHO), earlier supposed to be aluminium fluoride hydrate, was also found in Hekla fumaroles from the 1991 eruption, but its genetic relation with topsøeite remains unclear. Topsøeite is named after the family of Danish prominent scientists and industrialists including Haldor Topsøe the elder (1842–1935), Haldor Topsøe the younger (1913–2013) and Henrik Topsøe (1944).

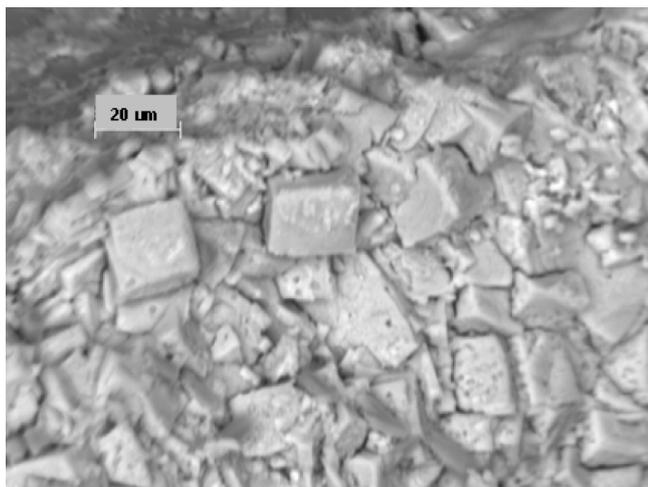
Key-words: topsøeite; new mineral; fluoride; iron fluoride hydrate; polymorphs; fumarole; Hekla; Iceland.

1. Introduction

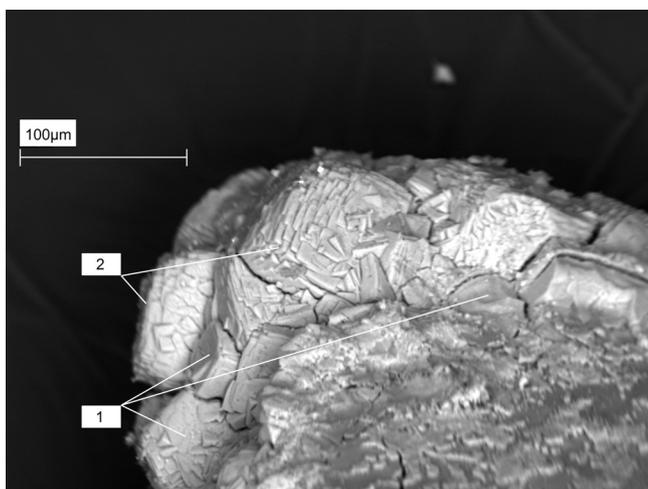
Hekla is one of the most active volcanoes on Iceland, with 18 eruptions during historic times. In 1991 it had an eruption that lasted from January to March. The volcanic activity was mainly restricted to a single fissure trending east-southeast from the top of the mountain. The most prolific area with respect to encrustations was on the eruption fissure above the main crater at 1105 m a.s.l. The lavas, the main crater and the linear eruption fissure cooled down to ambient temperatures at the surface in less than ten years (Balić-Žunić *et al.*, 2016). The sample containing topsøeite was collected on September 16, 1992 by Sveinn P. Jakobsson from the Icelandic Institute of Natural

History. During our expedition to Hekla in 2007 we could conclude that the fumaroles of the 1991 eruption had been covered by scoria of the subsequent 2000 eruption.

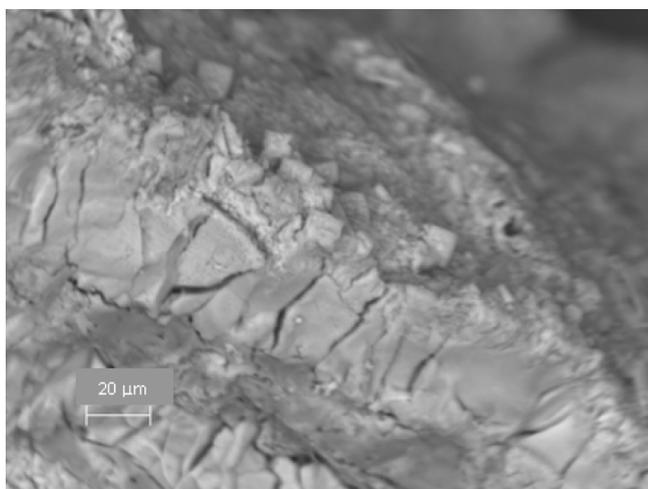
A preliminary description of topsøeite was given by Jakobsson *et al.* (2008) where the mineral was labelled HI (UM2008-30-F:FeHO). In addition to topsøeite, in the same paper a number of potentially new minerals were reported, some of which have been approved as new minerals (Balić-Žunić *et al.*, 2009, 2012 and 2017a; Garavelli *et al.*, 2010; Mitolo *et al.*, 2013), others are still under investigation. Topsøeite is named after the family of Danish scientists with three prominent individuals who made significant contributions to crystallography and chemistry during the last two centuries.



(a)



(b)



(c)

Fig. 1. Scanning electron microscope images: a) square-prismatic crystals of topsøeite, b) stepped crystal aggregates of topsøeite (1) associated with resembling aggregates of hematite crystals (2), c) massive veins of topsøeite with square-prismatic crystals on top.

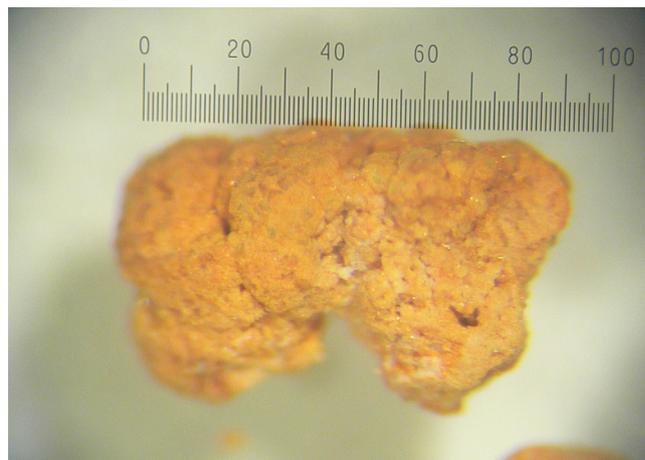


Fig. 2. Photograph of the fragment of sample NI 15515. Aggregate of topsøeite crystals mixed with mineral HD (Jakobsson *et al.*, 2008). One division on the scale corresponds to 20 μm .

Haldor Topsøe, the elder (Haldor Frederik Axel Topsøe) (1842–1935) was the first Danish crystallographer in the modern sense of this word. He started his career as assistant for G. Forchhammer at the Mineralogical Museum in Copenhagen and later in his career was director for the cryolite mine and company based in Ivittuut, Greenland and Copenhagen. He was internationally known for his work in chemistry and crystallography (*e.g.* his investigations of isomorphism) and in his home country was renowned for his contribution to the development of modern industry and improvement of working conditions and protection measures for workers. His mother, Sigrid Christine Gudrun, was of an Icelandic origin (born Thorgrimsen).

Haldor Topsøe (1913–2013) the younger, grandson of Haldor Topsøe the elder, was a renowned Danish chemist and industrialist. He devoted his life to the development of heterogeneous catalysis for the chemical industry and was the founder of Haldor Topsøe A/S Catalyst Company that to this day produces some of the best catalysts in the world and contributes to the world's welfare, *e.g.* through optimizing the fabrication of ammonia for the fertilizer industry.

Henrik Topsøe (b. 1944), the son of the former, is a renowned Danish chemist. He made significant contributions to the science of catalysis through the introduction of new scientific tools and concepts with a pronounced scientific and technological impact (*e.g.* in the development of hydrodesulphurisation).

The mineral and its name have been approved by the IMA Commission on New Minerals Nomenclature and Classification, IMA No. 2016-113 (Balić-Žunić *et al.*, 2017b). Holotype material is kept in the mineral collection of the Icelandic Institute of Natural History, Gardabaer, Iceland, under sample number NI 15515.

2. Occurrence and physical properties

Topsøeite forms short, pseudocubic tetragonal prisms up to several tens of μm in diameter, crystal aggregates of up to $100\ \mu\text{m}$, or formless fractured veins (Fig. 1) inside up to 3 mm thick yellow to brown crust on altered scoria, together with hematite, opal, malladrite, heklaite, ralstonite (hydrokenoralstonite after the new nomenclature of minerals in the pyrochlore supergroup) and several other still not fully characterized minerals (Fig. 2). The temperature in the fumarole at the time of sampling was 170°C . The mineral is of a yellow colour and most probably has no prominent cleavage, because only irregular fractures are apparent under the scanning electron microscope (SEM, Fig. 1) and no effect of preferred orientation could be noted on the reflection intensities in the powder X-ray diffraction (PXRD). The calculated density of the mineral is $2.067\ \text{g}\cdot\text{cm}^{-3}$, based on empirical formula, and $2.330\ \text{g}\cdot\text{cm}^{-3}$, based on the ideal formula. The experimental determination of the density could not be made due to the minute size of mineral grains in admixture with other phases. As the chemical analysis gives a deficiency of water, which we can explain only by limitations of the experimental method, we consider the value based on the crystal structure refinement more reliable and representative for the mineral. The measurement of optical properties was hindered by the intimate admixture with other minerals and to the minute size of the crystals. Taking into account the density based on the ideal formula, the calculated mean refractive index of topsøeite, using the Gladstone-Dale constants of Mandarino (1976, 1981) is 1.63.

3. Chemical composition

As typical for fumarolic deposits and especially for Hekla fumaroles (Balić-Žunić *et al.*, 2016), the sample containing topsøeite is a very porous, friable aggregate of micrometre-sized crystals of several intimately mixed minerals. From such material it is very difficult to obtain usable polished samples and the best choice for the chemical analysis appeared to be energy-dispersive spectroscopy (EDS) coupled to SEM on the sample in original morphology. Eleven point analyses were obtained by SEM-EDS (15 kV, 500 pA, $3\ \mu\text{m}$ beam diameter, 2500 cps average count rate, counting time 100 s). The instrument used was an S 360 Cambridge SEM coupled with an Oxford-Link Ge ISIS energy-dispersive spectrometer equipped with a Super Atmosphere thin window, since this allows better detection of light elements. The investigated part of the sample consisted of a 20–30 μm thick vein exposing relatively flat surfaces (Fig. 1c). Analyses were obtained using a lower than usual probe current due to the small analysed area. As we had to measure unpolished uneven surfaces, a “non-critical” working distance was utilized (Ruste, 1979; Acquafredda & Paglionico, 2004). The sample was sputtered with a 30 nm thick carbon film before analysis. The X-ray

Table 1. Topsøeite chemical data (in wt%).

Constituent	Mean	Range	esd	Standard
Fe	38.52	33.50–42.92	3.34	almandine
F	38.23	33.20–43.67	3.48	synth. LiF
Cl	1.03	0.41–1.64	0.42	halite
O	21.10	15.29–26.20	4.00	periclase
Total	98.88			

intensities were converted to wt% values by the ZAF4/FLS quantitative analysis software support of Oxford-Link Analytical (UK). Analytical data are given in Table 1. The empirical formula (based on Fe = 1 atom per formula unit) is $\text{Fe}(\text{F}_{2.94}\text{Cl}_{0.04})_{\Sigma 2.98}(\text{H}_2\text{O})_{1.94}$. The ideal formula is $\text{FeF}_3(\text{H}_2\text{O})_3$ which requires: Fe = 33.46, F = 34.15, O = 28.76 and H = 3.62 wt%.

4. Diffraction properties and crystal structure

The PXRD data (Table 2 and Fig. 3) were collected on a very small sample of topsøeite mixed with “mineral HD” (Jakobsson *et al.*, 2008) and small amounts of other phases. The instrument was a Bruker-AXS Advance 8 diffractometer with primary Ge_{111} monochromator and LynxEye silicon-strip detector. Geometry was reflection Bragg-Brentano and Cu $K\alpha_1$ radiation ($\lambda = 1.540596\ \text{\AA}$) was used. To avoid registering fluorescent radiation from the Fe-rich sample, the lower level for the detector window was adjusted to appropriate value. The sample was spread on a single-crystal “no background” quartz plate. The diagram matches well the data of synthetic β - $\text{FeF}_3(\text{H}_2\text{O})_3$ (Teufer, 1964; PDF 32-0464). For Table 2, positions and intensities of individual diffraction maxima were determined using the Bruker-AXS program EVA. The attribution of the maxima and the indexing were done in accordance with the results of the Rietveld refinement, which gave the crystallographic data presented in Table 3, compared to those of synthetic β - $\text{FeF}_3(\text{H}_2\text{O})_3$ (Teufer, 1964). Additional measurement and Rietveld refinement details are presented in Table 4.

The crystal structure of topsøeite, determined by Teufer (1964) on a synthetic sample using Weissenberg and precession photographs, consists of straight infinite chains of $[\text{FeF}_4(\text{H}_2\text{O})_2]$ octahedra extending along the *c* axis (Figs. 4 and 5). The adjacent octahedra share apical F atoms, whereas the four unshared, equatorially positioned atoms are represented by the disordered arrangement of two F and two O atoms from water molecules. The average composition of a chain is $[\text{FeF}_3(\text{H}_2\text{O})_2]$. Additional water molecules occupy the spaces between chains and are tetrahedrally coordinated by four (F, H_2O) from four different chains (indicated by thin bond lines on Fig. 5). The function of the inter-chain water molecules is obviously to bind the chains together through hydrogen bonds. As one third of the water molecules is not directly coordinated to Fe atoms but bonded only through

Table 2. X-ray powder diffraction data of topsøeite compared with the experimental diagram of synthetic β -FeF₃(H₂O)₃ (PDF 32-0464).

Topsøeite			β -FeF ₃ (H ₂ O) ₃		
<i>I</i> / <i>I</i> ₀ (%)	<i>d</i> _{meas.} (Å)	<i>d</i> _{calc.} (Å)	<i>hkl</i>	<i>I</i> / <i>I</i> ₀ (%)	<i>d</i> _{meas.} (Å)
100	5.55	5.54	1 1 0	100	5.54
43	3.92	3.92	0 2 0	55	3.92
9	3.87	3.87	0 0 1	14	3.88
39	3.47	3.47	0 1 1	50	3.48
22	3.17	3.17	1 1 1	25	3.18
30	2.77	2.77	2 2 0	30	2.77
8	2.60	2.60	1 2 1, 2 1 1	10	2.60
31	2.479	2.479	1 3 0, 3 1 0	30	2.475
13	2.087	2.087	1 3 1, 3 1 1	14	2.086
11	1.960	1.960	0 4 0	12	1.959
13	1.895	1.895	2 3 1, 3 2 1	14	1.895
16	1.877	1.877	0 1 2	25	1.882
17	1.849*	1.847	3 3 0	6	1.847
2	1.826	1.826	1 1 2	3	1.830
24	1.753	1.753	2 4 0, 4 2 0	25	1.751
9	1.707	1.706	1 4 1, 4 1 1	8	1.706
6	1.693	1.693	1 2 2, 2 1 2	9	1.696
		1.667	3 3 1	3	1.667
6	1.596*	1.596	2 4 1, 4 2 1	3	1.596
2	1.554	1.554	0 3 2	2	1.557
5	1.538	1.537	5 1 0, 1 5 0	5	1.536
		1.525	1 3 2, 3 1 2	2	1.527
3	1.453	1.453	4 3 1, 3 4 1, 0 5 1	3	1.452
8	1.445	1.445	2 3 2, 3 2 2	9	1.447
3	1.429	1.428	5 1 1, 1 5 1	3	1.428
9	1.362*	1.362	5 2 1, 2 5 1	4	1.362
7	1.356	1.356	1 4 2, 4 1 2	8	1.357
3	1.344	1.344	5 3 0, 3 5 0	2	1.343
4	1.288	1.289	0 0 3		
3	1.240	1.239	6 2 0, 2 6 0	3	1.239
4	1.218	1.218	4 3 2, 3 4 2, 0 5 2	4	1.218
3	1.163	1.163	5 2 2, 2 5 2		

* overlapped reflection

Table 3. Comparison of the crystallographic parameters of synthetic β -FeF₃(H₂O)₃ and topsøeite**.

Crystal system	Tetragonal			
Space group	<i>P</i> 4/ <i>n</i>			
<i>a</i> (Å)	7.846			
	7.8381(3)			
<i>c</i> (Å)	3.877			
	3.8674(1)			
<i>V</i> (Å ³)	238.67			
	237.60(2)			
<i>Z</i>	2			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Fe	0	1/2	0.145(1)	1.29(7)
			0.145(3)	1.3
F1	0	1/2	0.642(4)	1.3(3)
			0.661(7)	1.3
O1	0	0	1/2	1.7(2)
				2
F2, O2	0.2246(9)	0.3975(9)	0.139(2)	2.1(1)
	0.247(1)	0.387(1)	0.154(5)	2

* Teufer (1964) single-crystal analysis from Weissenberg and precession photographs

** This work, powder-data Rietveld analysis

hydrogen bonds, it might be assumed that the crystal structure can be partially dehydrated without collapsing and this would explain the deficit of the water obtained through the chemical analysis. However, it is difficult to imagine a complete dehydration of the inter-chain water leading to the formula FeF₃(H₂O)₂ without severe structural changes, because the framework of the [FeF₄(H₂O)₂] coordination polyhedra is not three-dimensionally connected without additional water molecules. Due to this argument and the results of structure refinement that show no deficit of inter-chain water, we assume that the amount of water measured by SEM-EDS method is not realistic, due to possibly induced dehydration under the electron bombardment, and the main reason for departure of the empirical structural formula from the ideal one is in this intrinsic limitation of the SEM-EDS method. Topsøeite (β -FeF₃(H₂O)₃) is isostructural to rosenbergite (β -AlF₃(H₂O)₃). There is an obvious mistake in the article of Teufer in the sign of the *z* coordinate of the mixed (F, H₂O) site: it should be negative, not positive as published. Together with a new choice of the asymmetric unit, this error is corrected and, besides, the new atomic parameters give improved values of bond distances. The

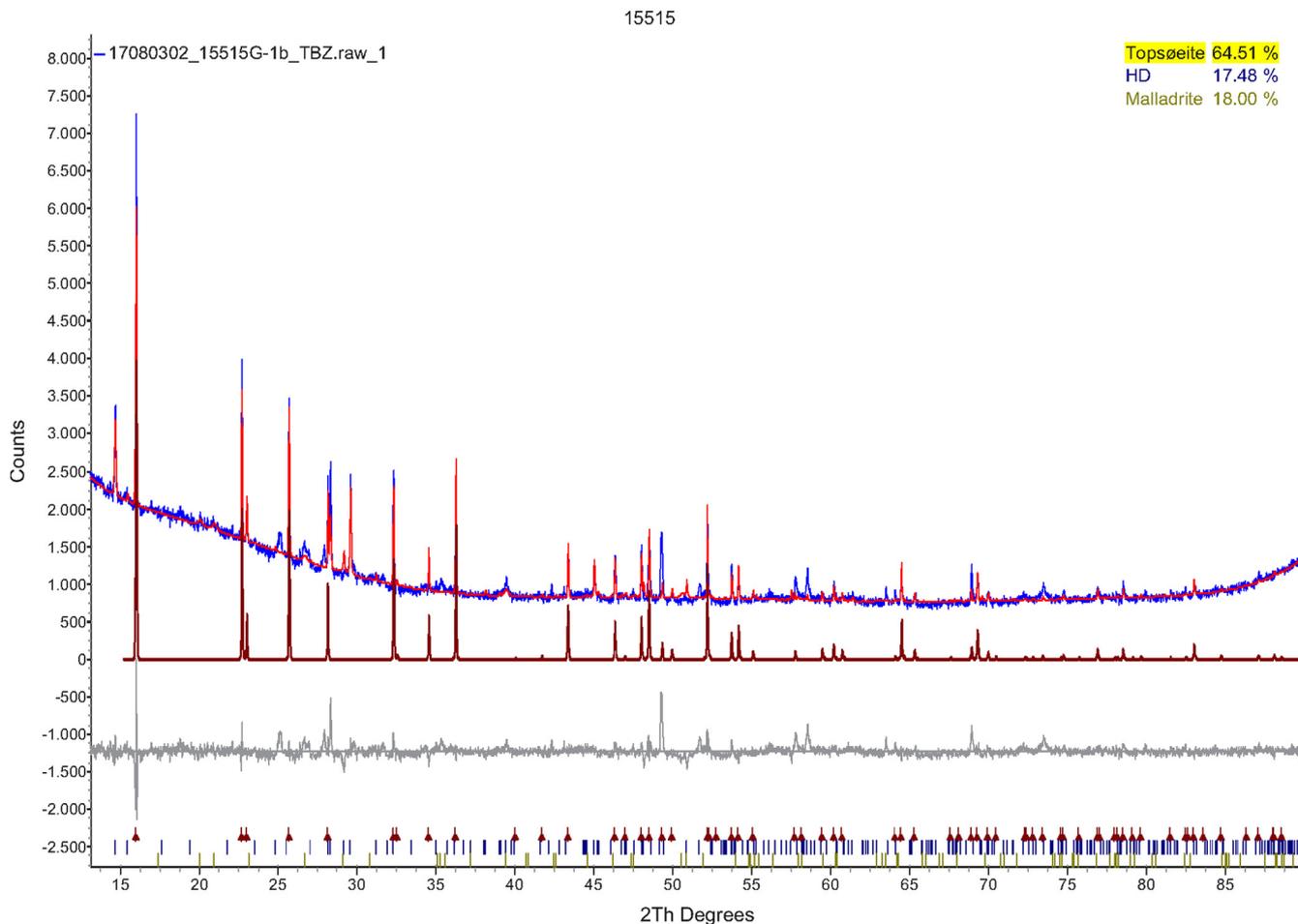


Fig. 3. XRPD diagram of topsøeite in mixture with “mineral HD” (Jakobsson *et al.*, 2008), malladrite and possibly small amounts of other phases, with the results of Rietveld refinement (Topas 4.1). Blue, experimental diagram; red, calculated diagram; grey, difference; brown: calculated pattern of topsøeite. Marks at the bottom indicate the expected positions of diffraction maxima.

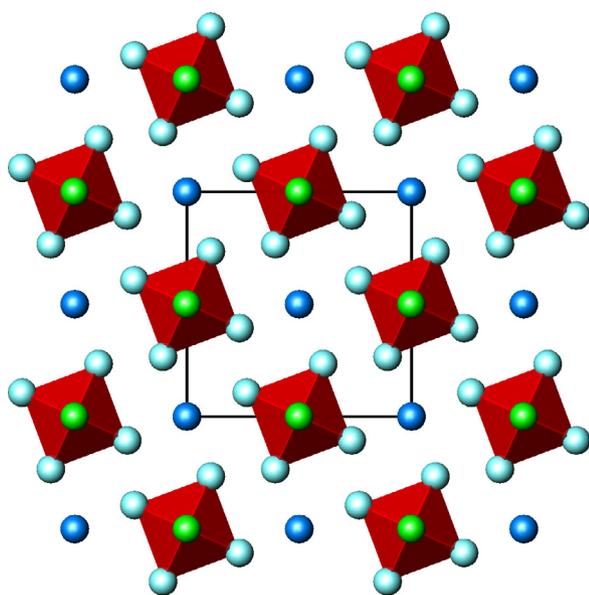


Fig. 4. Projection of the crystal structure of topsøeite along $[001]$. Fe coordination polyhedra are red, F1 atoms green, O1 atoms blue and mixed F2/O2 sites light blue (cyan).

coordination of Fe^{3+} in topsøeite is unique among iron fluorides hydrates. In all other examples (Table 5) Fe^{3+} is coordinated only by F atoms, whereas Fe^{2+} appears in mixed F+ H_2O coordinations. In $\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$ and $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$ it is a coordination with the same stoichiometry as in topsøeite [$\text{FeF}_4(\text{H}_2\text{O})_2$] but with four shared F atoms occupying the equatorial plane and the two H_2O groups at unshared apices. In $\text{FeF}_2(\text{H}_2\text{O})_4$ Fe^{2+} is coordinated by two F and four H_2O groups with a disordered arrangement of F and H_2O on all vertices. The average bond length between Fe and apical F atoms in topsøeite is 1.934 Å, which is in accordance with the Fe^{3+} -F bond lengths in other Fe fluorides from Table 5, which range from 1.926 Å in $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$ to 1.946 Å in $\text{Fe}_3\text{F}_9(\text{H}_2\text{O})$. There is, though, a significant difference between the lengths of the two Fe-F bonds in topsøeite which are 1.872 and 1.996 Å, respectively. The F atom that makes shorter bond to Fe lies closer to the (001) plane of inter-chain H_2O molecules (Fig. 5). In the isostructural rosenbergite the difference between two Al-F bonds is much smaller (1.820 vs. 1.828 Å). At the same time, the distance between the inter-chain H_2O and equatorial (F, H_2O) from Fe/Al coordination octahedra (bridged by the hydrogen bonds) is

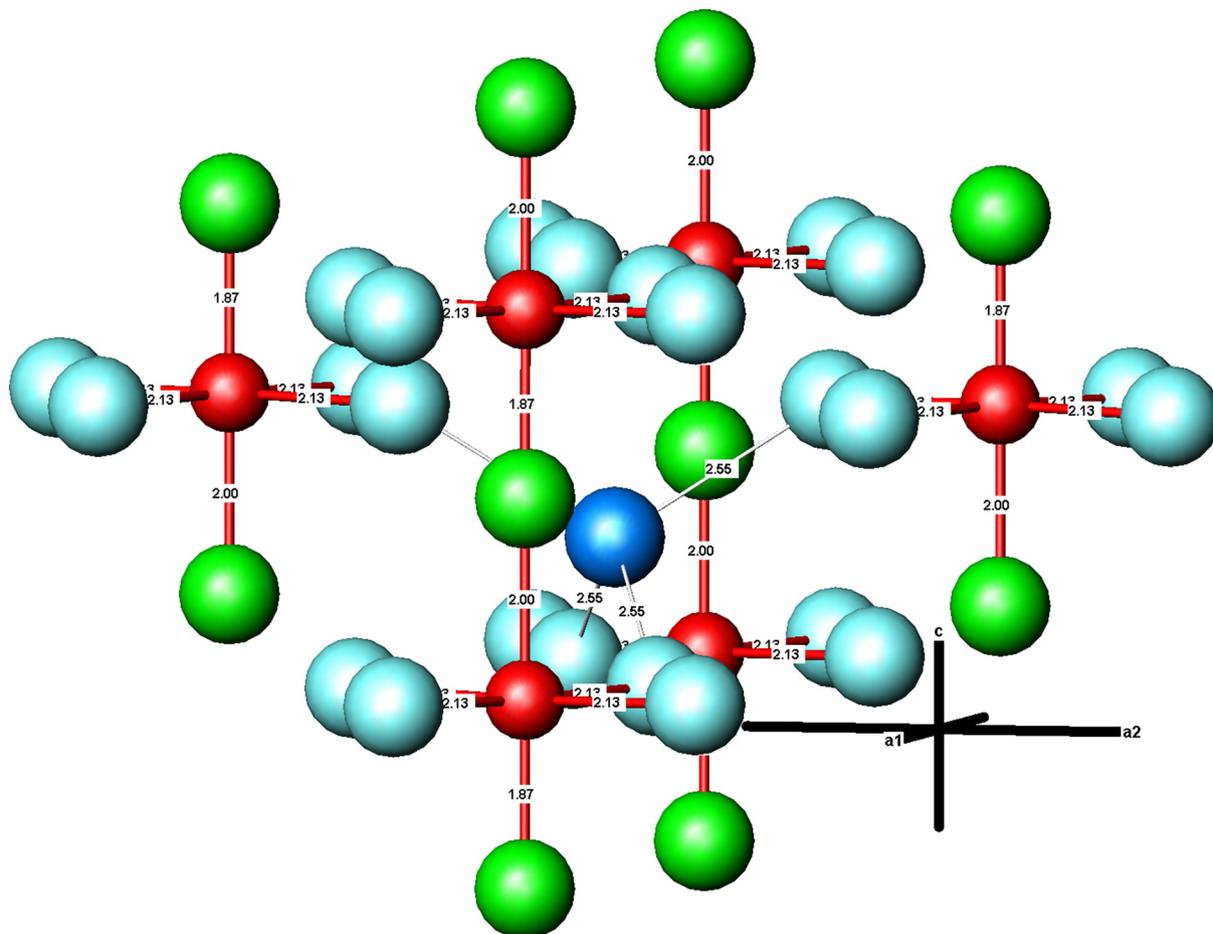


Fig. 5. Bonding details in the crystal structure of topsøeite. The bond-length values are in Å; the colouring of atoms as in Fig. 4.

Table 4. Rietveld refinement details.

Global parameters	
2 θ range (°)	13–90
Step scan (°2 θ)	0.02
Profile fitting type	fundamental parameters
Divergence slit	fixed (0.45°)
Background and amorphous modelling	Chebyshev polynomials
R _P	3.98%
R _{WP}	5.93%
R _E	3.04%
GOF	1.95
<i>Topsøeite parameters</i>	
R _B	4.14%
Calculated average crystallite size	> 1 μ m

significantly shorter in topsøeite (2.551 Å) than in rosebergite (2.676 Å). The bond distance between Fe and equatorial mixed (F, H₂O) sites in topsøeite is 2.129 Å, significantly longer than the apical Fe–F bond distances.

5. Relation to other minerals

To the best of our knowledge, topsøeite is the first iron fluoride hydrate fully described from nature. Rosenbergite, which is isostructural with topsøeite, is likewise the only well-described natural aluminium fluoride hydrate so far. However, in the phase systems Fe–F–H₂O and Al–F–H₂O, there are several other known synthetic phases (Table 5).

Several of the different Al and Fe fluorides have Al or Fe atoms coordinated by both F and H₂O. Among them, only those with stoichiometry MF₃(H₂O)₃ have isostructural representatives with both Al and Fe variant. There are two structural varieties (polymorphs) with this stoichiometry and they are represented by a tetragonal form (rosenbergite and topsøeite) and a rhombohedral form. Whereas the crystal structures of rosenbergite and topsøeite consist of infinite straight chains of interconnected coordination octahedra of Al or Fe with additional inter-chain water molecules, in the rhombohedral polymorphs the coordination octahedra of Al or Fe are isolated and all their vertices have mixed occupancy of 1:1 F and H₂O.

Table 5. Crystal-structure data of iron and aluminium fluoride hydrates.

Formula	S.G.	Lattice parameters	Structure type	Octahedral framework	References
$\text{Fe}_3\text{F}_9(\text{H}_2\text{O})$	<i>Cmcm</i>	7.423, 12.730, 7.526 Å	hexagonal tungsten bronze	3D framework with broad channels occupied by H_2O	Le Blanc <i>et al.</i> , 1983
$\text{Al}_2(\text{F},\text{OH})_6(\text{H}_2\text{O})$	<i>Fd-3m</i>	9.8614 Å	pyrochlore	3D framework with channels occupied by H_2O	Fourquet <i>et al.</i> , 1988
$\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$	<i>C2/m</i>	7.609, 7.514, 7.453 Å, 118.21°	“shifted hexagonal bronze type”	3D framework, 1/3 of octahedra with two unshared vertices occupied by H_2O	Le Blanc <i>et al.</i> , 1984
$\text{AlF}_3(\text{H}_2\text{O})$	<i>Pm-3m</i>	3.61 Å	perovskite	3D framework, H_2O in large cavities	Chandross, 1964
$\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$	<i>Imma</i>	7.477, 10.862, 6.652 Å	anti-weberite	3D framework, 1/2 of octahedra with two unshared vertices occupied by H_2O	Laligant <i>et al.</i> , 1986
$\text{FeF}_3(\text{H}_2\text{O})_3$ (topsøeite)	<i>P4/n</i>	7.846, 3.877 Å	rosenbergite	infinite chains with four unshared corners as mixed (F, H_2O), the rest of H_2O between chains	Teufer, 1964
$\text{AlF}_3(\text{H}_2\text{O})_3$ (rosenbergite)	<i>P4/n</i>	7.715, 3.648 Å	isostructural with the former	isostructural with the former	Olmi <i>et al.</i> , 1993
$\text{FeF}_3(\text{H}_2\text{O})_3$ (mineral HU: Jakobsson <i>et al.</i> , 2008)	<i>R-3m</i>	9.260, 4.687 Å	rhombohedral $\text{AlF}_3(\text{H}_2\text{O})_3$	isolated octahedra, all vertices mixed (1/2 F, 1/2 H_2O). The structure is disordered, with two “twin” orientations of octahedra, according to the operation of the m plane.	data from preliminary research
$\text{AlF}_3(\text{H}_2\text{O})_3$	<i>R-3m</i>	9.205, 4.654 Å	isostructural with the former	isostructural with the former	Kemnitz <i>et al.</i> , 2006
$\text{FeF}_2(\text{H}_2\text{O})_4$	<i>R-3m</i>	9.50, 4.82 Å	isotypic with the former	isolated octahedra with mixed vertices (1/3 F, 2/3 H_2O). The structure is disordered, with two “twin” orientations of octahedra, according to the operation of the m plane.	Penfold & Taylor, 1960
$\text{AlF}_3(\text{H}_2\text{O})_9$	<i>R-3</i>	11.085, 8.042 Å	rhombohedral $\text{AlF}_3(\text{H}_2\text{O})_3$ with additional H_2O	isolated octahedra with mixed (F, H_2O) occupancy of all vertices with additionally 2/3 of H_2O in interstices.	Ilyukhin & Petrosyants, 2002

It is interesting that both polymorphs of $\text{FeF}_3(\text{H}_2\text{O})_3$ have been found in Hekla fumaroles. They correspond to the minerals HI (topsøeite) and HU (UM2008-27-F: AlHO) of Jakobsson *et al.* (2008). In the latter work, HU was supposed to be the rhombohedral polymorph of $\text{AlF}_3(\text{H}_2\text{O})_3$. However, a SEM-EDX analysis (our unpublished data) proves it to be the Fe phase. Both Fe fluorides are relatively rare minerals in Hekla fumaroles, topsøeite being found with certainty in only one of the collected samples and HU in only two. However, in the

samples where they have been found, they are fairly well represented. It is particularly interesting that they are not observed together. There are at present no clear clues about what determines the formation of one or the other polymorph in the fumaroles, but for the aluminium equivalents the rhombohedral form is reported to be a metastable one, which at room temperature or elevated temperatures (90 °C) readily transforms to the tetragonal form (Kemnitz *et al.*, 2006). In Hekla samples we did not observe a transformation of HU to topsøeite. Their

paragenesis is similar as regards the dominating phases in the samples (ralstonite, malladrite, heklaite). Topsøeite appears in well-developed crystals associated with hematite, which in the chemical analyses showed a possible presence of around 3 at% F and 2.5 at% Cl. Fluorine-doped $\alpha\text{Fe}_2\text{O}_3$ is known from syntheses (*e.g.* Wang *et al.*, 2017). The observed association (Fig. 1b) might suggest formation of topsøeite through transformation of hematite in the acidic, fluorine-rich aqueous environment through the reaction: $\text{Fe}_2\text{O}_3 + 6\text{HF} + 3\text{H}_2\text{O} \rightarrow 2\text{FeF}_3(\text{H}_2\text{O})_3$

Contrary to topsøeite, which appears in distinct crystals, its polymorph HU has not been observed with a clear morphology but only as a base on which the potentially new mineral HT (UM2008-31-F:FeHOSi; Jakobsson *et al.*, 2008) with composition $\text{FeSiF}_6(\text{H}_2\text{O})_6$ grows in aggregates of small crystals.

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References

- Acquafredda, P & Paglionico, A. (2004): SEM-EDS microanalyses of microphenocrysts of Mediterranean obsidians: a preliminary approach to source discrimination. *Eur. J. Mineral.*, **16**, 419–429.
- Balić-Žunić, T., Garavelli, A., Acquafredda, P., Leonardsen, E., Jakobsson, S.P. (2009): Eldfellite, $\text{NaFe}(\text{SO}_4)_2$, a new fumarolic mineral from Eldfell volcano, Iceland. *Mineral. Mag.*, **73**, 51–57.
- Balić-Žunić, T., Garavelli, A., Mitolo, D., Acquafredda, P., Leonardsen, E. (2012): Jakobssonite, CaAlF_5 , a new mineral from fumaroles at the Eldfell and Hekla volcanoes, Iceland. *Mineral. Mag.*, **76**, 751–760.
- Balić-Žunić, T., Garavelli, A., Jakobsson, S.P., Jonasson, K., Katerinopoulos, A., Kyriakopoulos, K., Acquafredda, P. (2016): Fumarolic Minerals: An Overview of Active European Volcanoes. in “Updates in Volcanology – From Volcano Modelling to Volcano Geology”, K. Nemeth, ed., InTech, Rijeka, 267–322, <http://dx.doi.org/10.5772/64129>.
- Balić-Žunić, T., Garavelli, A., Pinto, D., Mitolo, D. (2017a): Verneite, IMA 2016-112. CNMNC Newsletter No. 36, April 2017. *Eur. J. Mineral.*, **29**, 339–344.
- Balić-Žunić, T., Garavelli, A., Mitolo D. (2017b): Topsøeite, IMA 2016-113. CNMNC Newsletter No. 36, April 2017. *Eur. J. Mineral.*, **29**, 339–344.
- Chandross, R. (1964): The structure of a new phase of aluminium trifluoride monohydrate. *Acta Crystallogr.*, **17**, 1477–1478.
- Fourquet, J.L., Rivière, M., Le Bail, A., Nygren, M., Grins, J. (1988): Crystal structure and protonic conductivity of pyrochlore phases $\text{Al}_2((\text{OH})_{1-x}\text{F}_x)_6 \cdot \text{H}_2\text{O}$ and $\text{Al}_2((\text{OH})_{1-x}\text{F}_x)_6$ ($x = 0.5$). *Eur. J. Solid State Inorg. Chem.*, **25**, 535–540.
- Garavelli, A., Balić-Žunić, T., Mitolo, D., Acquafredda, P., Leonardsen, E., Jakobsson, S.P. (2010): Heklaite, KNaSiF_6 , a new fumarolic mineral from Hekla volcano, Iceland. *Mineral. Mag.*, **74**, 147–157.
- Ilyukhin, A.B. & Petrosyants, S.P. (2002): Aluminium fluoride nanohydrate. *Kristallografiya*, **47**, 631–633. (*Crystallography Reports*, 47(4), 574–576.)
- Jakobsson, S.P., Leonardsen, E.S., Balić-Zunic, T., Jonsson, S.S. (2008): Encrustations from three recent volcanic eruptions in Iceland: The 1963–1967 Surtsey, the 1973 Eldfell and the 1991 Hekla eruptions. *Fjölrít Náttúrufræðistofnunar*, **52**, 65.
- Kemnitz, E., Gross, U., Ruediger, S., Scholz, G., Heidemann, D., Troyanov, S.I., Morosov, I.V., Lemee-Cailleau, M.H. (2006): Comparative structural investigation of aluminium fluoride solvates. *Solid State Sci.*, **8**, 1443–1452.
- Laligant, Y., Pannetier, J., Labbe, P.H., Ferey, G. (1986): A new refinement of the crystal structure of the inverse weberite $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$. *J. Solid State Chem.*, **62**, 274–277.
- Le Blanc, M., Ferey, G., Chevalier, P., Calage, Y., de Pape, R. (1983): Hexagonal Tungsten Bronze-Type Fe(III) Fluoride: $(\text{H}_2\text{O})_{0.33}\text{FeF}_3$; Crystal structure, magnetic properties, dehydration to a new form of iron trifluoride. *J. Solid State Chem.*, **47**, 53–58.
- Le Blanc, M., Ferey, G., Calage, Y., de Pape, R. (1984): Idle spin behavior of the shifted hexagonal tungsten bronze type compounds $\text{FeFe}_2\text{F}_8(\text{H}_2\text{O})_2$ and $\text{MnFe}_2\text{F}_8(\text{H}_2\text{O})_2$. *J. Solid State Chem.*, **53**, 360–368.
- Mandarino, J.A. (1976): The Gladstone-Dale relationship. I. Derivation of new constants. *Can. Mineral.*, **14**, 498–502.
- (1981): The Gladstone-Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.*, **19**, 441–450.
- Mitolo, D., Garavelli, A., Balić-Žunić, T., Acquafredda, P., Jakobsson, S.P. (2013): Leonardsenite, $\text{MgAlF}_5(\text{H}_2\text{O})_2$, a new mineral species from Eldfell Volcano, Heimaey Island, Iceland. *Can. Mineral.*, **51**, 377–386.
- Olmi, F., Sabelli, C., Trosti-Ferroni, R. (1993): Rosenbergite, $\text{AlF}(\text{F}_{0.5}(\text{H}_2\text{O})_{0.5})_4(\text{H}_2\text{O})$, a new mineral from the Cetine mine (Tuscany, Italy): description and crystal structure. *Eur. J. Mineral.*, **5**, 1167–1174.
- Penfold, B.R. & Taylor, M.R. (1960): The crystal structure of a disordered form of iron(II) fluoride tetrahydrate. *Acta Crystallogr.*, **13**, 953–956.
- Ruste J. (1979): X-Ray spectrometry. in “Microanalysis and Scanning Electron Microscopy”, F. Maurice, L. Meny, R. Tixier, ed., Les Editions de Physique, Orsay, 215–267.
- Teufer, G. (1964): The crystal structure of β iron(III) trifluoride trihydrate, $\beta\text{-FeF}_3 \cdot 3\text{H}_2\text{O}$. *Acta Crystallogr.*, **17**, 1480.
- Wang, C., Zhang, Y., Li, Y., Liu, J., Wu, Q., Jiang, J., Li, Y.Y., Jian Lu, J. (2017): Synthesis of fluorine-doped $\alpha\text{-Fe}_2\text{O}_3$ nanorods toward enhanced lithium storage capability. *Nanotechnology*, **28**, 065401.

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