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Jakobssonite, $CaAlF_5$, a new mineral from fumaroles at the Eldfell and Hekla volcanoes, Iceland

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ABSTRACT

The new mineral jakobssonite, ideally $CaAlF_5$, was first found in crusts collected in 1988 from a fumarole on the Eldfell volcano, Heimaey Island, Iceland. It was subsequently found in similar crusts collected in 1991 from a fumarole on the Hekla volcano, Iceland. It is associated with leonardsenite (IMA2011-059), ralstonite, heklaite, anhydrite, gypsum, jarosite, hematite, opal and several fluoride minerals that have not been fully characterized. Jakobssonite occurs as soft white fragile crusts of acicular crystals <50 μm long. Its calculated density is 2.89 g cm^{-3}. Chemical analyses by energy-dispersive spectrometry on a scanning electron microscope produced a mean elemental composition as follows: Ca, 18.99; Al, 18.55; Mg, 1.33; Na, 0.33; F, 50.20; O, 10.39; total 99.79 wt.%. The empirical chemical formula, calculated on the basis of 7 atoms per formula unit with all of the oxygen as OH, is $(Ca_{0.73}Mg_{0.09}Na_{0.02})_{\Sigma 0.84}Al_{1.06}F_{4.09}(OH)_{1.01}$. Jakobssonite is monoclinic, space group $C2/c$, with a = 8.601(1), b = 6.2903(6), c = 7.2190(7) Å, β = 114.61(1)°, V = 355.09(8) Å^3 and Z = 4. The crystal structure contains chains of $[AlF_6]$ octahedra which run parallel to the c axis. These chains are interconnected by chains of $[CaF_7]$ pentagonal bipyramids. Jakobssonite is isostructural with several other $CaM^{III}F_5$ compounds. The eight strongest lines in the powder diffraction diagram [d in Å (I) (hkl)] are as follows: 4.91 (18) (110), 3.92 (76) (200), 3.15 (68) (020), 3.13 (100) $(1\bar{1}\bar{2})$, 2.27 (22) $(2\bar{2}\bar{2})$, 1.957 (21) (400), 1.814 (20) $(1\bar{3}\bar{2})$, 1.805 (22) $(20\bar{4})$. The chemical and crystal-structure analyses of jakobssonite are similar to synthetic $CaAlF_5$ with minor substitutions of light elements (e.g. Na) or vacancies for Ca, and OH for F.

Keywords: jakobssonite, new mineral, fumaroles, sublimates, fluoride, Eldfell, Hekla, Iceland.

Introduction

The fumaroles on the Eldfell and Hekla volcanoes in Iceland have a rich and diverse mineralogy (Balić-Žunić *et al*., 2009; Garavelli *et al*., 2010). Sulphates and fluorides are the most common minerals (Jakobsson *et al*., 2008). This work describes a new fluoride mineral which was the second most abundant after ralstonite in the fumaroles at Eldfell in the 1980s and 1990s and at Hekla following the eruption in 1991. Jakobssonite was first reported as a potentially new mineral on the basis of powder diffraction data by Jakobsson *et al*. (2008), who referred to it as 'mineral HA'. In the list of unnamed minerals maintained by the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) (Smith and Nickel, 2007), it is listed in the invalid minerals under the code UM2008-//-?[5].

The new mineral and its name have been approved by the CNMNC (IMA 2011-036;

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Balić-Žunić *et al.*, 2011). The name honours Sveinn Peter Jakobsson (1939–), one of Iceland's leading volcanologists, in acknowledgement of his major contributions to research on Icelandic fumaroles, and because he was the first person to recognize it.

The most common occurrence of the mineral was at Eldfell where it crystallized in post-eruptional fumarole encrustations following the 1973 eruption (Thorarinsson *et al.*, 1973). A specimen collected on 30th April 1988 on the northeast rim of the main volcanic crater (locality 5 in fig. 9 and specimen NI 12256 of Jakobsson *et al.*, 2008) has been designated as the holotype as it was the first to be collected. The mineral has been identified on five further specimens from the same locality, collected on subsequent expeditions on 5th July 1990 and 15th November 1995. Jakobssonite has also been identified in fumarole encrustations on Hekla, which formed following the 1991 eruption (Gudmundsson *et al.*, 1992); these include one specimen collected at Breiarskar on 12th July 1991 (which has been designated as a cotype specimen), and twenty specimens collected on 16th September 1992 and on 15th September 1993 in the fissure above the eastern main volcanic crater. The presence of jakobssonite has been confirmed recently on specimens collected on Eldfell on a field trip in August 2009. It is still forming in the Eldfell fumaroles but in smaller quantities relative to other fluoride minerals.

The holotype specimen of jakobssonite is preserved in the mineral collection of the Icelandic Institute of Natural History, Reykjavík, Iceland, as specimen number NI 12256 (Eldfell). The cotype specimen has the number NI 15511 (Hekla). Other specimens in the same collection which contain jakobssonite are NI 13554, NI 20625, NI 20626, NI 20627, NI 20630 (Eldfell); and NI 15206, NI 15505, NI 15506, NI 15507, NI 15508, NI 15509, NI 15512, NI 15513, NI 15514, NI 15518, NI 15519, NI 15520, NI 17063, NI 17064, NI 17067, NI 17068, NI 17069, NI 17071, NI 17072, NI 17077 (Hekla).

Mineral paragenesis

On the holotype specimen from Eldfell volcano, jakobssonite occurs as acicular crystals up to 50 µm long in association with granular leonardsenite, $MgAlF_5{\cdot}2H_2O$ (Figs 1 and 2), another mineral that has recently received IMA approval (Mitolo *et al.*, 2011). Jakobssonite occurs as a white overgrowth on a yellowish base of massive ralstonite, anhydrite and jarosite which together form a 2–3 cm thick crust on altered scoria of hawaiitic composition. In other specimens from the same locality jakobssonite is associated with ralstonite, gypsum, hematite, anhydrite, opal-A and several as yet uncharacterized minerals. The temperature of the fumarole is ~230ºC.

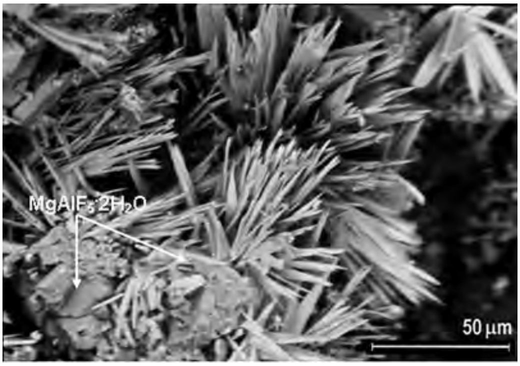

FIG. 1. A SEM image of acicular jakobssonite crystals in association with granular leonardsenite, $MgAlF_5{\cdot}2H_2O$, from the holotype specimen, NI 12256, from Eldfell volcano.

On the cotype specimen from Hekla volcano, jakobssonite occurs as aggregates of crystals that are less than a micrometre in size. It forms white crusts up to a few millimetres thick, intergrown or associated with leonardsenite, heklaite, malladrite, hieratite, fluorite, chiolite, phases with the formulae $Na_2Ca_3Al_2F_{14}$ and $FeSiF_6{\cdot}6H_2O$ and

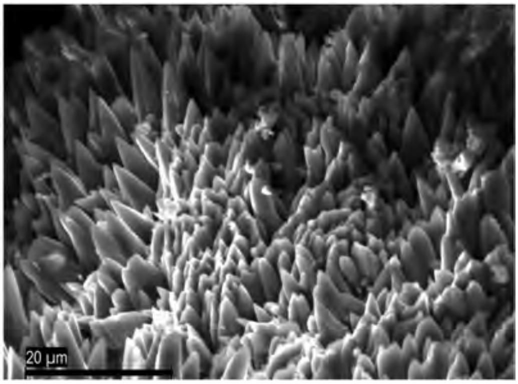

FIG. 2. A high magnification SEM image of an aggregate of jakobssonite crystals from the holotype specimen, NI 12256, from Eldfell volcano.

other as yet uncharacterized minerals, typically covering ralstonite, on altered andesitic scoria (Jakobsson *et al*., 2008). The measured temperature of the Hekla fumarole varied between 155 and 333ºC. This locality, which was rich in jakobssonite, was covered by scoria during the 2000 eruption at Hekla as revealed by a recent visit to the crater (Garavelli *et al*., 2010).

On the basis of the relative abundance of jakobssonite on the samples on which it was identified, we conclude that it is the second most abundant fluoride after ralstonite in the fumarole sublimates on Eldfell and Hekla in their initial active stages.

Physical properties

Jakobssonite occurs as acicular crystals (Figs 1 and 2) which are probably elongated along [100], the direction of the structural chains of Al and Ca coordination polyhedra (see below). It is white and due to the minute crystal size the macroscopic lustre is earthy. The crystals are transparent and do not fluoresce in long-wave ultraviolet light. The small crystal size did not allow a determination of hardness or optical properties and the intimate mixture with other minerals prevented an experimental determination of the density. Unfortunately, the optical properties of the synthetic $CaAlF_5$ do not appear to have been reported. The density calculated from the empirical formula and unit-cell parameters is 2.89 g cm^{-3}.

Chemical composition

An S 360 Cambridge scanning electron microscope (SEM) with an Oxford-Link Ge ISIS energy-dispersive spectrometer (EDS) and a Super Atmosphere thin window, which allows better detection of light elements, was used to determine the composition. An EDS was chosen for quantitative analyses of the crystals in preference to a wavelength-dispersive spectrometer, due to the improvements in specimen stability provided by lower beam currents. The investigated specimen consisted of an aggregate of crystals typically 10 to 15 μm in size (Figs 1–3).

The investigations were carried out on a polished thin section (Fig. 3) coated with a 30 nm carbon film prior to the observations and analyses. Accurate analyses of small volumes were obtained by using a low probe current and a 'non-critical' working distance (Ruste, 1979; Acquafredda and Paglionico, 2004). The operating conditions were 15 kV accelerating potential, 500 pA probe current, with 2500 counts per second as the average count rate across the whole spectrum and typical counting times of 100 s. The X-ray intensities were converted to wt.% elements by *ZAF4/FLS* quantitative analysis software provided by Oxford-Link Analytical (UK). The procedure allows the sample peak heights and areas to be compared with standards, and it takes the relative contribution of the matrix and partial or complete overlaps of peaks produced by different elements into account.

The compositional data (means of 25 analyses from the holotype specimen) are listed in Table 1. The empirical formula (based on 7 atoms per formula unit) is $(Ca_{0.73}Mg_{0.09}Na_{0.02})_{\Sigma 0.84}Al_{1.06}F_{4.09}(OH)_{1.01}$. An ideal composition with a formula $CaAlF_5$ requires Ca = 24.73, Al = 16.65 and F = 58.62 wt.%; $CaAlF_4OH$ requires Ca = 25.04, Al = 16.86, F = 47.48, O = 10.00 and H = 0.63 wt.%.

Crystal Structure

The X-ray powder diffraction data (Table 2) were collected on a Bruker AXS D8 diffractometer in Bragg–Brentano geometry with a primary beam Ge(111) monochromator, using Cu$K\alpha_1$ radiation (λ = 1.5406 Å) and a fixed divergence slit. It proved impossible to separate a pure sample, all of the powder patterns were mixtures with other

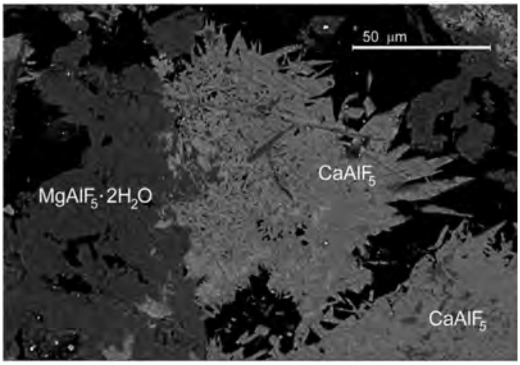

FIG. 3. A polished section imaged by SEM of the fragment of holotype specimen NI 12256 from Eldfell volcano used for the chemical analysis. Jakobssonite, ideally $CaAlF_5$, is associated with leonardsenite, $MgAlF_5 \cdot 2H_2O$.

TABLE 1. Analytical data for jakobssonite from the holotype specimen, NI 12256, from Eldfell volcano.

Constituent	Mean (wt.%)	Range	SD	Standard used	$CaAlF_5$*	$CaAlF_4OH$‡
Ca	18.99	18.04–20.16	0.63	Wollastonite	24.73	25.04
Mg	1.33	0.99–1.85	0.23	Periclase		
Na	0.33	0.18–0.58	0.10	Albite		
Al	18.55	18.01–19.01	0.27	Corundum	16.65	16.86
F	50.20	49.23–51.18	0.47	Synthetic LiF	58.62	47.48
O	10.39	9.76–10.95	0.37	Periclase		10.00
Total	99.79					

* Required for $CaAlF_5$.
‡ Required for $CaAlF_4OH$.

minerals. The positions and intensities of diffraction maxima were determined using the Bruker-AXS program *EVA*. The attribution of the maxima and indexing were done by Rietveld refinement using the Bruker AXS program *Topas 4*. A carefully selected white subsample from the cotype specimen NI 15511 from Hekla was chosen for the Rietveld refinement as it contained the largest amount of the new mineral (70 wt.%) and ralstonite was the only major contaminant. There was a very small amount of hieratite (<1 wt.% according to the Rietveld refinement) and traces of one or more other minerals in the analysed powder. This specimen provided the diffraction pattern reported in Table 2 and shown in Fig. 4. The crystal-lattice parameters are listed in Table 3. Somewhat different lattice parameters were obtained from the holotype specimen (Eldfell, NI 12256) suggesting possible substitution in the crystal structure (these are also listed in Table 3) but less jakobssonite was present in this specimen and it was intergrown with several other phases with a larger pattern overlap, which makes these data less reliable (see below).

The final atom parameters for jakobssonite from Hekla (the cotype specimen) are listed in Table 4,

TABLE 2. X-ray powder diffraction data from the cotype specimen, NI 15511, of jakobssonite from Hekla volcano compared to data for synthetic α-$CaAlF_5$.

Jakobssonite				Synthetic $CaAlF_5$‡	
I/I_0 (%)	d_{meas} (Å)	d_{calc} (Å)	*hkl*	I/I_0 (%)	d_{meas} (Å)
24	5.74		*R*		
18	**4.91**	**4.90**	**110**	1	4.93
7	*4.72*		*H*		
4	4.54	4.54	$1\bar{1}\bar{1}$	5	4.59
4	*4.33*		*?*		
4	*4.25*		*?*		
76	**3.92**	**3.91**	**200**	100	3.95
4	3.53	3.51	111	2	3.54
9	3.28	3.28	$002/20\bar{2}$	1	3.33
68	**3.15**	**3.15**	**0 2 0**	47	3.16
100	**3.13**	**3.13**	$\mathbf{1\bar{1}\bar{2}}$	83	3.18
15	*3.00*		*R*		
17	*2.88*		*R*		
2	2.61	2.61	$3\bar{1}\bar{1}$	0.1	2.64
2	2.53	2.52	$2\bar{2}\bar{1}$	0.1	2.54
			310	3	2.43

TABLE 2 (*contd*.).

Jakobssonite				Synthetic $CaAlF_5$[‡]	
I/I_0 (%)	d_{meas} (Å)	d_{calc} (Å)	*hkl*	I/I_0 (%)	d_{meas} (Å)
3	*2.35*		*H*		
11*	2.283	2.271	022	19	2.291
22	**2.270**	**2.268**	**$2\bar{2}\bar{2}$**		
9	2.228	2.226	$1\bar{1}\bar{3}$	7	2.260
			$40\bar{2}$	1	2.14
5	2.064	2.061	$3\bar{1}\bar{3}$	5	2.096
15*	2.027	2.025	130	4	2.035
		2.023	311	2	2.040
14	1.998	1.997	$1\bar{3}\bar{1}$	10	2.008
21	**1.957**	**1.955**	**400**	28	1.973
			$2\bar{2}\bar{3}$	1	1.922
9	*1.913*		*R*		
			131	3	1.889
			113	2	1.849
20	**1.814**	**1.813**	**$1\bar{3}\bar{2}$**	20	1.827
22	**1.805**	**1.805**	**$20\bar{4}$**	21	1.837
14*	1.757	1.756	222	11	1.770
		1.752	$4\bar{2}\bar{2}$		
6	1.693	1.692	$3\bar{3}\bar{1}$	4	1.704
5	*1.681*		*R*		
14	1.660	1.661	312	13	1.674
		1.660	420		
		1.656	$5\bar{1}\bar{2}$	9	1.677
7	1.640	1.646	132	4	1.657
		1.644	$3\bar{3}\bar{2}$		
		1.641	004	6	1.665
		1.636	$40\bar{4}$	6	1.667
3	1.587	1.582	$5\bar{1}\bar{3}$	2	1.606
10*	1.574	1.573	040	6	1.579
9	1.566	1.565	$2\bar{2}\bar{4}$	10	1.588
			$1\bar{3}\bar{3}$		
			041	1	1.537
6*	1.498	1.497	331	3	1.506
			421	1	1.501
3	1.459	1.459	240	2	1.466
4	1.418	1.418	$042/2\bar{4}\bar{2}$	1	1.427
4	*1.391*		*R*		
6	1.329	1.331	332	4	1.340
		1.329	204	6	1.344
		1.328	$5\bar{3}\bar{2}$	4	1.340
		1.324	$60\bar{4}$	4	1.346
4	1.224	1.225	440	4	1.233
		1.224	224	3	1.236
		1.220	$6\bar{2}\bar{4}$	3	1.238
4	1.187	1.188	$1\bar{5}\bar{2}$	2	1.195
		1.186	$2\bar{4}\bar{4}$	3	1.198
		1.185	$3\bar{3}\bar{5}$	3	1.202

The eight strongest jakobssonite reflections are listed in bold.

The reflections of ralstonite (*R*) and suspected hieratite (*H*) plus one or more unidentified phases (*?*) are listed in italics.

* Reflections overlapping with those of ralstonite.

[‡] From PDF 04-007-7072 (Hemon and Courbion, 1991).

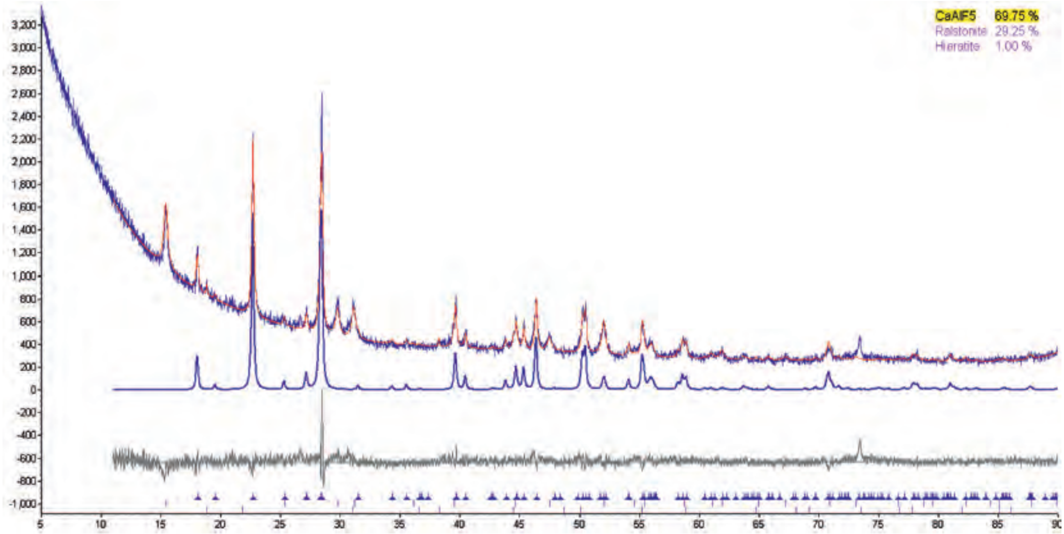

FIG. 4. X-ray powder-diffraction pattern of a mixture of jakobssonite and ralstonite from the cotype specimen, NI 15511, from Hekla volcano. The observed (blue) and calculated (red) curves are shown together with a difference curve (grey) and the theoretical jakobssonite pattern calculated by Rietveld refinement (middle blue curve). Output from program *Topas 4*.

the full details of the Rietveld refinement and the experimental diffraction pattern have been deposited with the Principal Editors of *Mineralogical Magazine* and are available at www.minersoc.org/pages/e_journals/dep_mat.html

The successful Rietveld refinement, starting from the crystal structure of synthetic $CaAlF_5$ (Hemon and Courbion, 1991), converged to an agreement index, R_{wp}, of 6.5%. It is monoclinic, space group $C2/c$, with a = 8.601(1), b = 6.2903(6), c = 7.2190(7) Å, β = 114.61(1)°, V = 355.09(8) Å^3 and Z = 4. There are minor differences from the synthetic compound. Jakobssonite has slightly smaller unit-cell para-

TABLE 3. Crystal-lattice parameters of jakobssonite compared to synthetic $CaAlF_5$ and other structurally related fluorides. For $FeAlF_5$ the lattice parameters were transformed from orthorhombic *Immm* to the monoclinic $C2/c$ setting.

Compound	a (Å)	b (Å)	c (Å)	β (°)	References
Jakobssonite from NI 15511	8.601(1)	6.2903(7)	7.2190(7)	114.61(1)	This work
Jakobssonite from NI 12256	8.685(2)	6.280(1)	7.341(1)	115.5(1)	This work
$CaAlF_5$	8.712(3)	6.317(2)	7.349(3)	115.04(3)	Hemon and Courbion (1991)
$CaCrF_5$	9.005(5)	6.472(5)	7.533(5)	115.8(1)	Kun Wu and Brown (1973)
$FeAlF_5$	8.2367(8)*	6.203(1)	7.115(1)**	115.59***	Fourquet *et al.* (1994)

* Calculated from Fourquet *et al*. (1994) as $(a_O^2 + c_O^2)^{½}$.
** Calculated from Fourquet *et al*. (1994) as $2c_O$.
*** Calculated from Fourquet *et al*. (1994) as $90° + \tan^{-1}(c_O/a_O)$.

TABLE 4. Atom parameters of jakobssonite from specimen NI15511 from Hekla.

Site	Multiplicity	x/a	y/b	z/c	Occupancy	B (Å^2)*
Ca1	4	0	0.544(2)	¼	0.66(1)	0.55
Al1	4	0	0	0	1	0.5
F1	4	0	0.950(3)	¼	1	1.1
F2	8	0.034(1)	0.720(2)	0.988(2)	1	1
F3	8	0.770(2)	0.968(2)	0.870(2)	1	1.3

* Constrained to values from Hemon and Courbion (1991).

meters (Table 3) as a result of the shorter Ca−F distances (Table 5) and the Ca occupancy factor refines to less than 1 in specimen NI 15511 from Hekla (Table 4).

The lattice parameters of the holotype specimens from Eldfell (NI 12256) are closer to those of synthetic $CaAlF_5$ (Table 3) and the Rietveld refinement did not suggest low occupancy at the Ca site in this specimen. However, the specimen from Eldfell contains a smaller proportion of jakobssonite and the characteristic {110} reflection overlaps with leonardsenite, $MgAlF_5{\cdot}2H_2O$, which dominates the diffraction pattern. This reflection is particularly important, because the lower occupancy of the Ca site for the sample from Hekla is exactly the structural feature which explains its unexpectedly high intensity in this sample. The lower occupancy factor could be explained by substitution by a lighter element (such as Na or Mg), by structural vacancies, or a combination of both. The results of the chemical analyses suggest that the last explanation is the most probable. A Ca for Na substitution and vacancies at the Ca site would be in accord with the experimental chemical formula. As this would introduce a deficit in the cation valences it is possible that some of the oxygen atoms substituting for fluorine are present as H_2O rather than OH. It has not been possible to determine which of the F sites in the structure are influenced by the substitution. It is not likely to be the bridging F1 site in the Al−F chains (Fig. 5) but one or both of the other sites. A H_2O for F substitution would require that some of the

TABLE 5. Coordination parameters for Al and Ca in the crystal structure of jakobssonite in comparison to synthetic α-$CaAlF_5$ (Hemon and Courbion, 1991).

	Jakobssonite	α-$CaAlF_5$
Ca−F3 (2×)	2.11(1)	2.207(1)
Ca−F2 (2×)	2.31(1)	2.293(1)
Ca−F2 (2×)	2.31(1)	2.349(1)
Ca−F1	2.56(2)	2.526(1)
Mean bond length	2.29(15)	2.32(11)
Eccentricity (%)	14.1	14.8
Asphericity (%)	17.4	10.0
Volume distortion (%)	4.4	2.7
Al−F2 (2×)	1.79(1)	1.749(1)
Al−F3 (2×)	1.82(1)	1.806(1)
Al−F1 (2×)	1.832(3)	1.873(1)
Mean bond length	1.814(16)	1.809(56)
Eccentricity (%)	0	0
Asphericity (%)	2.7	9.2
Volume distortion (%)	0.3	0.3
Al−F−Al (°)	157.5	157.5

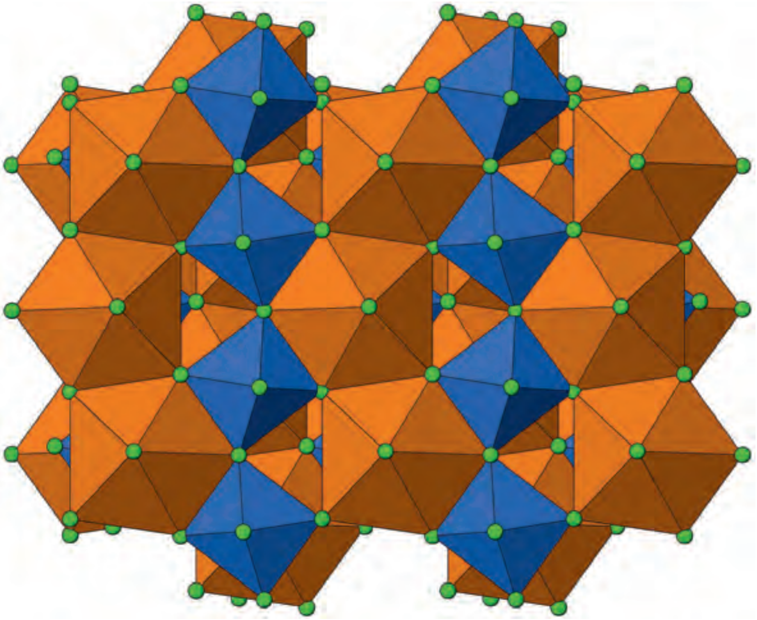

FIG. 5. Projection of the jakobssonite structure on (100), with the *c* axis vertical. The [AlF_6] coordination polyhedra are blue and the [CaF_7] are orange.

ligands in the [AlF_6] octahedra are replaced by water molecules, an unusual but not impossible structural feature. For example, heptahydrates with the general formula [$M(II)(H_2O)_6$] [$AlF_5(H_2O)$] contain disordered isolated [$AlF_4(F,H_2O)_2$] coordination octahedra (Adamczyk *et al.*, 2000). We have been unable to determine the substitution mechanism in the structure of jakobssonite due to a lack of suitable crystals, however our results suggest significant compositional variability with departure from the ideal formula in some specimens.

The crystal structure of $CaAlF_5$ contains isolated chains of [AlF_6] octahedra parallel to the *c* axis. These chains are interconnected by chains of pentagonal [CaF_7] bipyramids (Fig. 6). Each Ca−F chain bridges four Al−F chains. Unlike the Al−F chains, Ca−F chains link along two of the equatorial edges. The [CaF_7] polyhedra are embedded between the [AlF_6] octahedra in such a manner that the equatorial plane of the bipyramid joins pairs of adjacent octahedra in two of the chains and they share apical F atoms with the two octahedra from two additional chains (Figs 5 and 6). The pentagonal bipyramids are formed by a distortion of octahedral coordination by the approach of an additional F atom in the equatorial plane. This is the bridging atom in the Al−F chain and therefore a kink in the Al−F chain is produced (Fig. 5). This F1 atom has the longest bond to Ca (2.56 Å as compared to 2.11−2.31 Å for the other six atoms, Table 5).

The Al coordination is fairly regular, with no eccentricity of the central cation and with only 2.7% volume asphericity in the arrangement of F atoms and a very small volume distortion of 0.3%. The Ca coordination is much more distorted compared to a regular pentagonal bipyramid. The largest discrepancy of 17.4% is in the volume asphericity of the F atoms. The volume eccentricity of the central cation is 14.1%; whereas the volume distortion is only 4.4%, with distortion parameters calculated according to Balić-Žunić (2007). The values are only slightly different to those of synthetic α-$CaAlF_5$ (Hemon and Courbion, 1991).

Relationship to similar mineral and synthetic phases

The CaF_2−AlF_3 system at atmospheric pressure has three ternary phases, the high and low temperature polymorphs of $CaAlF_5$, and Ca_2AlF_7 (Craig and Brown, 1977; Body *et al.*, 2005). None of these, to the best of our knowledge, has been reported previously as a naturally occurring phase.

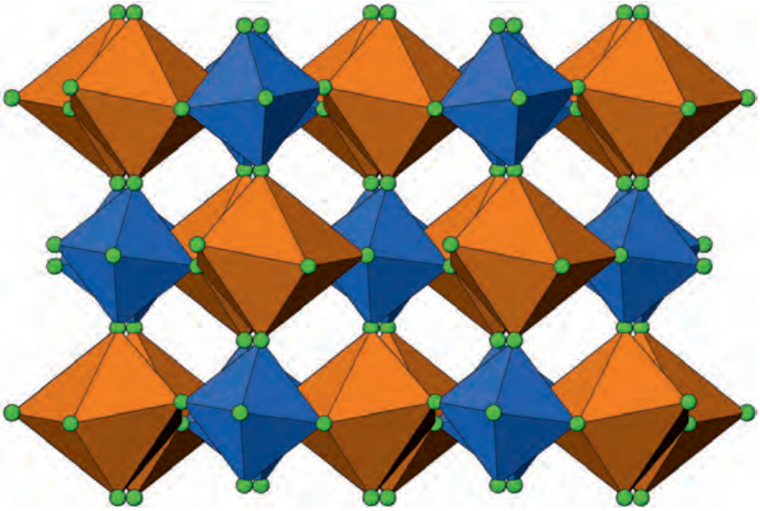

FIG. 6. Projection of the jakobssonite structure along the *c* axis (*b* axis horizontal).

Jakobssonite is identical (apart from minor substitutions) to low-temperature α-$CaAlF_5$, which is the stable polymorph at temperatures <740ºC (Hemon and Courbion, 1991; Body *et al.*, 2005). This substance is isostructural with a number of $CaM^{III}F_5$ compounds in which M = Cr, Ti, V, Co and Ga (Dumora *et al.*, 1971; Kun Wu and Brown, 1973). All of these have monoclinic *C*2/*c* structures which are derived from the orthorhombic *Immm* $FeAlF_5$ structure (Fourquet *et al.*, 1994) by kinking of the Al–F chains and a concomitant transformation of the octahedral coordinations of adjacent chains to pentagonal bipyramids as described above. In contrast to $CaAlF_5$, anhydrous $MgAlF_5$ has an undeformed $FeAlF_5$ structure (Weil and Werner, 2001).

The high-temperature β-form of $CaAlF_5$ (Body *et al.*, 2005) contains the same types of parallel Al–F and Ca–F chains as the α-form but they are connected in a different way and this phase is isostructural with $CaFeF_5$ (Graulich *et al.*, 2003). These monoclinic $P2_1/c$ structures are, in turn, developed by a distortion of the orthorhombic $MnAlF_5$ structure (Ferey *et al.*, 1993). In these cases the distortion also causes an increase in the coordination sphere of Ca to pentagonal bipyramidal from the octahedral coordination of Mn. The Al–F chains are kinked in all of the structures, but slightly less so in $MnAlF_5$.

In contrast to the $CaAlF_5$ polymorphs, Ca_2AlF_7 contains isolated $[AlF_6]$ octahedra in a framework of $[CaF_7]$ and $[CaF_8]$ polyhedra (Domesle and Hoppe, 1980). It has a slightly lower melting temperature than β-$CaAlF_5$ (845ºC compared to 873ºC) and is close in composition to the eutectic of the system (at 836ºC).

Prosopite, $CaAl_2(F,OH)_8$, and gearksutite, $CaAlF_4OH{\cdot}H_2O$, are the only other natural Ca–Al fluorides, they are found as alteration products of cryolite and in low temperature supergene environments. They have not been reported from fumaroles to the best of our knowledge.

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