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Verneite, $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$, a New Aluminum Fluoride Mineral from Icelandic and Vesuvius Fumaroles

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Abstract: Verneite, $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$, is a new mineral first discovered in fumarolic samples from both Hekla, Iceland and Vesuvius, Italy. Additional occurrences are so far from Eldfell and Fimmvörduhals, both on Iceland. Verneite is cubic, $I2_13$, $a = 10.264(1) \text{ \AA}$, $V = 1081.4(3) \text{ \AA}^3$, $Z = 4$, and corresponds to the known synthetic compound. The empirical formula is $\text{Na}_{2.01}\text{Ca}_{2.82}\text{Al}_{2.17}\text{F}_{14.02}$ (scanning electron microscopy with energy dispersive spectrometer from an unpolished sample). It appears in crystals up to 20 μm in diameter, with {110}, {100}, and {111} as the main forms. In the crystal structure of its synthetic analogue, Na is coordinated by 7 F atoms in the form of a capped octahedron, Ca with 8 F atoms in the form of a bisdisphenoid, and Al with 6 F atoms in the form of an octahedron. The crystal structure of $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ contains sinuous chains of Ca coordination polyhedra interlacing with similarly sinuous chains of Na coordination polyhedra and forming together with them layers parallel to {100}. The intersecting layers parallel to three equivalent crystallographic planes form a three-dimensional mesh with Al coordinations imbedded in its holes. The characteristics of Ca coordinations in fluorides, as well as their relations to other ternary Na–Ca–Al fluorides are discussed. Verneite is named after Jules Verne.

Keywords: verneite; new mineral; crystal structure; Hekla; Vesuvius; Eldfell; aluminofluoride

1. Introduction

The new mineral verneite, $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$, was discovered among sublimates collected from fumaroles on the Eldfell and Hekla volcanoes, where a considerable number of new fumarolic minerals has been observed [1]; six of them have so far been fully described [2–7]. The same mineral phase was identified at approximately the same time in a sublimate sample from Vesuvius, belonging to the Pelloux collection, which is stored in the mineralogical section of the Museum of Earth Sciences at Bari University. The original label of this Museum sample, with its 1925 date, indicates “Avogadrite from Vesuvius”.

Sveinn P. Jakobsson from the Icelandic Institute of Natural History collected the verneite type specimen on 16 September 1992 on Hekla. He also collected the cotype specimen from the Eldfell volcano in 1988. The holotype and the cotype are kept in the mineral collection of the Icelandic Institute of Natural History, Garðabær, Iceland, under sample numbers NI 15509 and NI 12256, respectively. The mineral was also registered in the samples NI 15518 and NI 17046 from Hekla, and NI 24457 and NI 24565 from Fimmvörduhals, kept in the same museum, and in samples E4-1A, E4-2A and E4-2B, collected on Eldfell in 2009 and presently kept at the Department of Geosciences and Natural Resource

Management of the University of Copenhagen. The Vesuvius sample is kept in the mineralogical collection of the Department of Earth and Geo-environmental Sciences, University of Bari.

Verneite is named after Jules Verne (1828–1905), the famous French author of novels, poetry, and plays, best known for his adventure novels and his profound influence on the literary genre of science fiction and, through it, the promotion of science, especially among young people. In his novel *Voyage au centre de la Terre* (1864), Verne describes a group of characters descending through a crater of a quiescent volcano in Iceland (Snæfell) and, after an adventurous journey through exciting Earth's underground, finally being ejected in South Italy with the eruption of a volcano (Stromboli). Therefore, we consider the name verneite appropriate for a mineral found and described by the same team of researchers on the best-known Icelandic and Italian volcanoes. Both the mineral and the mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification of the IMA (no. 2016-112).

In the present work, we give a detailed description of the occurrences of verneite, the morphological and chemical analysis by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), and the crystallographic analysis by Powder X-ray Diffraction (PXRD) and discuss its crystal structure details.

2. Materials and Methods

The geological settings and a description of the Hekla and Eldfell fumaroles where the new mineral was found are given in the papers mentioned in the Introduction [1–7]. Recently, the mineral has also been identified in samples originating from fumaroles on Fimmvörduhlás, Iceland, active during and after the eruption in 2010 [8]. Verneite occurs in medium to low temperature (170 °C at the time of sampling) fumaroles, as white-yellowish to brown crusts and massive aggregates up to several mm in size, sometimes also in transparent, colorless to pale yellowish crystals. In the sample from Eldfell, crystals up to 20 µm in diameter with a rhombic dodecahedral habit have been observed (Figure 1a), whereas in the Vesuvius sample, smaller (up to 10 µm) crystals having a combination of {100}, {110}, and {111} forms have been noted (Figure 1b). Verneite from Vesuvius was found during a reexamination of a sublimate sample belonging to the “Alberto Pelloux mineralogical collection”, housed at the “Palace of the Earth Sciences” of Bari University. The original label gives the following indication in Pelloux's own handwriting: “Avogadrite from Vesuvius collected on 15 July 1925—avogadrite or malladrite?” We conclude, therefore, that the mineral originates from fumaroles formed after the violent eruption of 1906, which was the last prior to the date reported in the label. Considering that avogadrite was discovered in 1926 by Professor Ferruccio Zambonini of Naples University, we conclude that the acquisition of the sample (from the well-known mineral salesman “Roberto Palumbo”, according to the indication on Pelloux's label) happened after 1926. As indicated on the label, Pelloux himself pointed to a need for further investigation of the sample. This was initially conducted by C.L. Garavelli and coworkers in the 1960s, who reported in it the presence of ralstonite, matteuccite, avogadrite, malladrite, and of a probably new mineral, $MgSiF_6 \cdot 6H_2O$, suitable for further studies (C.L. Garavelli, unpublished documents). We could not confirm this last phase during the present investigation.

Verneite in Hekla samples forms mixtures with ralstonite and hematite, sometimes also with jakobssonite and “mineral HB” [1] with a still unknown composition, but known PXRD data. The other minerals, which appear together with verneite in the type specimen and other samples from Hekla, are leonardsenite, heklaite, malladrite, opal, and fluorite. In the samples from Eldfell, where the cotype stems from, verneite is associated with jakobssonite, “mineral HB”, anhydrite, leonardsenite, ralstonite, jarosite, and meniaylovite. In the present investigation of the sample from Vesuvius, we found verneite associated with ralstonite and, to a lesser degree, to hieratite and knasibfite.

For the determination of the chemical composition, samples of verneite were analyzed by SEM-EDS. The Eldfell sample was analyzed by a S 360 Cambridge SEM, coupled with an Oxford-Link Ge ISIS EDS equipped with a Super Atmosphere thin window, whereas a 50XVP LEO SEM and

Oxford AZtec system with an Oxford SDD XMax (80 mm²) detector were used for the Vesuvius sample. The samples were sputtered with a 30 nm thick carbon film before analysis. As we had to measure inclined surfaces, a “noncritical” working distance was utilized [9,10]. X-ray intensities were converted to wt % values by the ZAF4/FLS quantitative analysis software support of Oxford-Link Analytical. For standards, we used synthetic LiF (F), albite (Na), wollastonite (Ca), corundum (Al), and orthoclase (K).

The crystallographic data were obtained by PXRD on diffractometers with Bragg–Brentano geometry, first the Panalytical (formerly Philips) PW3710 diffractometer with a long fine focus Cu sealed tube, secondary-beam graphite monochromator, and a variable-slit for the beam divergence. Subsequently, a Bruker-AXS D8 diffractometer with a ceramic Cu tube, primary-beam Ge111 monochromator, fixed divergence slit, and Lynx-Eye silicon strip detector was used. Bruker-AXS program Topas was used for the Rietveld refinement.

The crystallographic data for verneite and other compared crystal structures were calculated by program IVTON [11].

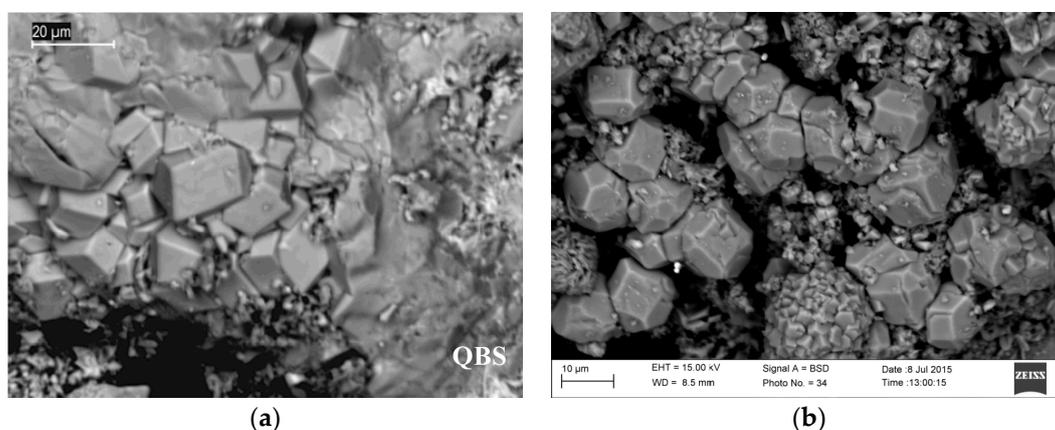


Figure 1. (a) SEM image of the crystals of verneite in association with fine-grained jakobssonite in the cotype sample from Eldfell. (b) SEM image of verneite crystals from the Vesuvius sample.

3. Results

3.1. Chemical Formula and Physical Properties

The empirical formulae (based on 7 cations *pfu*) are: $\text{Na}_{2.01}\text{Ca}_{2.82}\text{Al}_{2.17}\text{F}_{14.02}$ for the Eldfell sample and $(\text{Na}_{1.47}\text{K}_{0.09})_{\Sigma 1.56}\text{Ca}_{3.25}\text{Al}_{2.19}\text{F}_{14.33}$ for the Vesuvius sample. The ideal formula is $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$, which requires: F = 54.71, Na = 9.46, Ca = 24.73, and Al = 11.10 wt %.

The calculated density of verneite, from the empirical formula and the unit-cell data, is 2.974 g/cm³. The calculated refractive index using the Gladstone–Dale constants of Mandarino [12] is 1.357.

The cleavage, hardness, streak, and lustre of verneite could not be accurately determined due to the minute size of the crystals and the admixture with other minerals. No fluorescence was observed on the investigated samples, either under short-wavelength or long-wavelength ultraviolet radiation.

It could be expected that verneite is piezoelectric due to its space group symmetry.

3.2. Crystal Structure Data

Verneite is analogous to synthetic $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ investigated by Courbion and Ferrey [13]. It is cubic, $I2_13$, $a = 10.264(1)$ Å, $V = 1081.4(3)$ Å³, $Z = 4$. The atomic parameters and a list of bond lengths and angles are given in Reference [13].

Verneite was identified by PXRD in samples from all localities mentioned above. Rietveld refinements of verneite using the atomic parameters of Courbion and Ferrey [13] match the observed data very well in intensities. Due to this, and the fact that it was impossible to obtain a pure diagram of the mineral, which was always mixed with at least three other components in all the investigated

samples, a full crystal structure refinement from powder diffraction data, with the inclusion of atomic parameters, was not attempted. Table 1 presents the PXRD data for the sample from the type locality (Hekla), containing verneite, ralstonite, hematite, and jakobssonite, as well as a minor undetermined amount of the still not fully investigated “mineral HB” [1].

Table 1. X-ray powder diffraction data of verneite from Hekla (recorded with automatic variable divergence slit) compared with the experimental diagram of synthetic $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ (PDF 36-1496). HB = mineral HB [1]; R = ralstonite; J = jakobssonite; H = hematite.

hkl/Mineral	d (Å) ¹	I/I ₀ % ¹	d (Å) ²	I/I ₀ % ²
0 1 1	7.24	17.4	7.24	20
R	5.72	39.0	-	-
0 0 2	5.11	17.6	5.11	14
2 1 1	4.18	76.2	4.18	91
?	3.84	15.3	-	-
H	3.67	25.6	-	-
0 2 2	3.62	54.7	3.62	55
HB	3.54	22.4	-	-
?	3.30	25.6	-	-
0 3 1	3.23	68.1	3.24	60
HB, J	3.17	28.7	-	-
R	2.99	56.9	-	-
2 2 2	2.95	100.0	2.96	85
R	2.87	41.6	-	-
3 2 1	2.73	38.2	2.74	24
H	2.70	74.6	-	-
H	2.512	69.1	-	-
4 1 1	2.414	40.5	2.413	33
?	2.349	20.0	-	-
4 0 2	2.288	40.5	2.289	21
H	2.201	35.7	-	-
3 3 2	2.184	78.3	2.183	72
HB	2.127	20.5	-	-
4 2 2	2.088	20.2	2.090	5
R, J	2.042	22.1	-	-
3 4 1, 4 3 1	2.009	98.2	2.008	100
R	1.915	37.1	-	-
2 5 1	1.871	75.1	1.877	72
H	1.840	37.9	-	-
0 4 4	1.811	84.1	1.810	72
4 3 3 + R	1.755	40.5	1.756	9
0 0 6	-	-	1.708	7
H	1.697	51.3	-	-
6 1 1, 5 3 2, 3 5 2	1.663	66.2	1.661	55
0 6 2	-	-	1.620	1
H	1.607	23.0	-	-
4 5 1	1.582	28.4	1.581	8
6 2 2	1.545	45.9	1.544	38
3 6 1	1.512	30.6	1.510	10

¹ verneite Hekla. ² PDF 36-1496.

Table 2 gives the results of the Rietveld refinement. The refinement shows that the sample is made up by 53(1) wt % of verneite, 30(1) wt % of ralstonite, 15.9(6) wt % of hematite, and 1.6(4) wt % of jakobssonite, as well as a minor, not determined quantity of “mineral HB”.

Table 2. Rietveld refinement results. “Mineral HB” [1], also present in the sample, was not included in refinement because structural details are unknown. Average crystallite size modelled by Lorentzian function. Global parameters: $R_{\text{exp}} = 6.58\%$, $R_{\text{wp}} = 11.6\%$, $\text{GoF} = 1.76$, profile function: Fundamental parameters, background: Chebyshev polynomials.

	Verneite	Ralstonite	Hematite	Jakobssonite
average crystallite size (nm)	121(13)	35(2)	56(5)	fixed to 200
a (Å)	10.264(1)	9.963(2)	5.035(1)	8.63(3)
b (Å)	-	-	-	6.36(2)
c (Å)	-	-	13.824(4)	7.25(2)
β (°)	-	-	-	114.4(5)
atomic parameters	fixed [13]	fixed [14]	fixed [15]	fixed [4]
R-Bragg	4.7%	6.5%	5.8%	7.2%

4. Discussion

4.1. Description of the Crystal Structure

The original description of the crystal structure [13] presents it in an unconventional form as a combination of the cation-centered $[\text{AlF}_6]$ groups (octahedra) and anion-centered $[\text{FNaCa}_{3/2}]_2$ framework. This helps in relating the structure to some complex oxide structures presenting it as their “negative” (with the roles of cations and anions in frameworks exchanged), but ignores the coordinations of Na and Ca and makes the comparison with other fluorides difficult. Here, we give another view on the crystal structure, based solely on cation coordinations.

As expected from the Al:F ratio, verneite is an aluminofluoride with isolated $[\text{AlF}_6]$ octahedral groups and additional F atoms not bonded to Al. The arrangement of the six F atoms around the Al site is almost perfectly octahedral with a perfect sphericity [16] and a volume distortion (ν) [17] of only 0.0018. The Al atom sits on the three-fold axis 0.036 Å from the centroid of coordination, with eccentricity [16] of 0.0232. The average Al–F bond distance is 1.804 Å [13].

Ca atoms have an eight-fold coordination in the form of a bisdisphenoid (Figure 2). This type of coordination can achieve a configuration with the minimum ratio of the volume of a circumscribed sphere and the volume of the polyhedron for the coordination number 8; in other words, it is a maximum-volume polyhedron for this coordination number [18]. The Ca coordination polyhedron in verneite does not completely fulfill the conditions of a maximum-volume polyhedron because the four F atoms that form the shortened-disphenoid part of the coordination approach a square-planar arrangement (equatorial atoms on Figure 2). Consequently, its ν parameter (or volume distortion compared to the maximum-volume bisdisphenoid) is larger than zero (Table 3). This type of coordination is unique among the Ca–F coordinations in mineral fluorides and related synthetic compounds represented in Table 3.

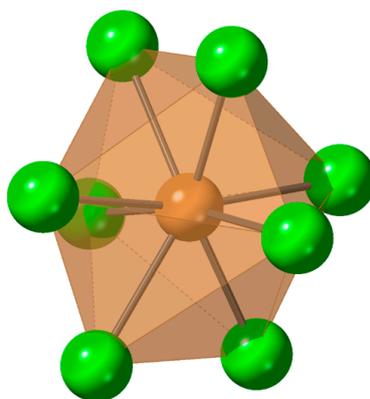


Figure 2. Bisdisphenoidal coordination of Ca in verneite. Projection based on crystal structure data from Reference [13].

Table 3. The coordination parameters of [CaF_n] coordination polyhedra in fluoride minerals and related synthetic compounds; ν = volume distortion; O. = Octahedron; P.b. = Pentagonal bipyramid; S.o. = Split octahedron; Bis. = Bisdisphenoid; S.a. = Square antiprism; C. = Cube; T.t.p. = Tricapped trigonal prism; T.c. = Tricapped cube.

Compound	Site	CN	<Ca–F> (Å)	ν	Asphericity	Eccentricity	Polyhedron	Ref.
CaLiAlF ₆	Ca1	6	2.281	0.0038	0	0	O.	[19]
Na ₄ Ca ₄ Al ₇ F ₃₃	Ca1	6	2.246	0.0232	0	0	O.	[20]
β -NaCaAlF ₆	Ca1	6	2.308	0.0439	0.0049	0.023	O.	[20]
KCaAl ₂ F ₉	Ca1	6	2.302	0.0703	0.0348	0.0165	O.	[21]
	Ca2	6	2.292	0.0559	0.0426	0.017		
CaAlF ₅	Ca1	7	2.318	0.0265	0.0335	0.0521	P.b.	[22]
Ca ₂ AlF ₇	Ca1	7	2.316	0.0344	0.0217	0.0248	P.b.	[23]
	Ca2	7	2.346	0.1391	0.0112	0.0404	S.o.	
α -NaCaAlF ₆	Ca1	7	2.351	0.0943	0.0331	0.054	transitional P.b./S.o.	[24]
	Ca2	7	2.343	0.0869	0.0405	0.0467		
Na ₂ Ca ₃ Al ₂ F ₁₄	Ca1	8	2.374	0.0234	0.0254	0.0286	Bis.	[13]
BaCaAlF ₇	Ca1	8	2.372	0.0467	0.0309	0.0361	S.a.	[25]
	Ca2	8	2.372	0.0569	0.0271	0.0362		
Ba ₂ CaMgAl ₂ F ₁₄	Ca1	8	2.371	0.0565	0.0453	0.0349	S.a.	[26]
Ca ₂ PbAlF ₉	Ca1	8	2.360	0.088	0.0181	0.0237	transitional C./S.a.	[27]
	Ca2	8	2.361	0.0899	0.0234	0.0241		
CaNa ₃ Mg ₃ AlF ₁₄	Ca1	8	2.421	0.1136	0.0583	0	distorted C.	[28]
CaF ₂	Ca1	8	2.365	0.1522	0	0	C.	[29]
Ca ₁₃ Y ₆ F ₄₃	Ca3	8	2.341	0.1444	0.021	0.0142	distorted C.	[30]
	Ca1*	9	2.617	0.0296	0.0627	0.0628	T.t.p.	
	Ca2	10	2.491	0.0478	0.0407	0.0576	T.c.	

The crystal structure data for the table are compiled from Reference [31]. As can be seen, the coordination number (CN) of Ca (coordinated with F atoms only) varies from 6 to 8 or even, rarely, 9 or 10. In the crystal structures with CN6, the coordination is in the form of a nearly perfect octahedron (in colquirite [19]) or subsequently more distorted octahedra in Na₄Ca₄Al₇F₃₃ [20], β -NaCaAlF₆ [20], and KCaAl₂F₉ [21]. Ca with CN7 appears in moderately distorted pentagonal bipyramids in jakobssonite [4,22] and Ca₂AlF₇ (Ca1) [23]. A regular pentagonal bipyramid is the maximum-volume polyhedron for CN7 and the ν values are calculated in comparison with it. Ca2 in Ca₂AlF₇ and the Ca coordinations in α -NaCaAlF₆ [24] have this parameter significantly different from zero because they represent a different type of coordination geometry, close to a “split octahedron”, the ideal form of which would have $\nu = 0.1333$ [17]. From values in Table 3, we can see that Ca2 in Ca₂AlF₇ closely approaches this form, whereas the coordinations in α -NaCaAlF₆ are transitional between a pentagonal bipyramid and a “split octahedron”. For CN8, the ideal types of coordination polyhedra are, in addition to bisdisphenoid, the cube (0.1522), the hexagonal bipyramid (0.0462), the square antiprism (0.0351), and the bicapped trigonal prism (0.0733). The numbers in parentheses are the ν values in comparison with the maximum-volume bisdisphenoid. The forms observed in Ca fluorides from Table 3 are a regular cube in fluorite and distorted cubes in tveitite (Ca3) [30] and coussellite [28]. The coordinations in calcioaravaipaite [27] are transitional between the cube and square antiprism, whereas the coordinations in usovite [26] and BaCaAlF₇ [25] are moderately distorted square antiprisms. In tveitite, the CN9 and CN10 Ca sites are also present. Ca1 with a tricapped trigonal prism coordination actually occupies a larger CN12 icosahedral void and is a split site, whereas the coordination of Ca2 can be described as a cube where one corner has been substituted by an F₃ triangle [30].

Na atoms have a seven-fold coordination with a capped octahedron as the coordination polyhedron (Figure 3). The capped octahedral face is broader than the opposite one (Figure 3).

The average Na–F bond distance is 2.431 Å [13], whereas the polyhedron distortion parameters are eccentricity = 0.0043, asphericity = 0.0615, and $\nu = 0.0849$ (compared to regular pentagonal bipyramid, which is the maximum-volume polyhedron for CN7). There is a considerably larger number of Na containing fluorides than those containing Ca, with a larger variability of coordination types; a comparative study of Na coordinations in fluorides will not be presented here, but in a special following article. We only mention that the Na coordination polyhedron type in verneite seems to be unique compared to other mineral fluorides, similar to the case of the Ca coordination polyhedron.

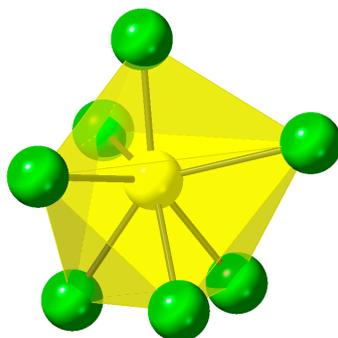


Figure 3. Na coordination in verneite. The three-fold axis is vertical. Projection based on crystal structure data from Reference [13].

The Ca coordination polyhedra build sinuous chains by sharing edges. They are interlaced by the sinuous chains of equally edge-sharing Na coordination polyhedra, and together these two types of chains build layers parallel to {100} (Figure 4). The layers, parallel to the three equivalent crystallographic planes, form a three-dimensional mesh that houses Al coordination octahedra in its interstices (Figure 5). The Al coordination octahedra share one face with a Na coordination polyhedron and three edges with Ca coordination polyhedra. Three F atoms at the corners that belong to the shared face are characterized by longer F–Al bonds (1.824 Å) and are each bonded to one Al, one Ca, and two Na. The three F atoms in the corners of the opposite face with shorter F–Al bonds (1.784 Å) make bonds to one Al and two Ca each. The directions of the sinuous chains of Ca and Na coordination polyhedra on the adjacent {100} faces, e.g., on the (100) and (010) faces, are mutually perpendicular (in this case [010] and [001], respectively), as required by the space group symmetry (Figure 5).

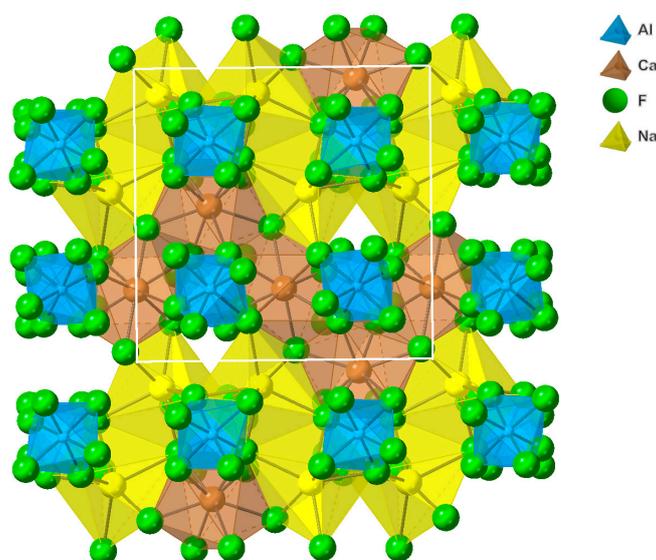


Figure 4. A {100} layer from the crystal structure of verneite, formed by sinuous chains of Ca coordinations and Na coordinations, and overlaid/underlain by the $[AlF_6]$ octahedra. Projection based on crystal structure data from Reference [13].

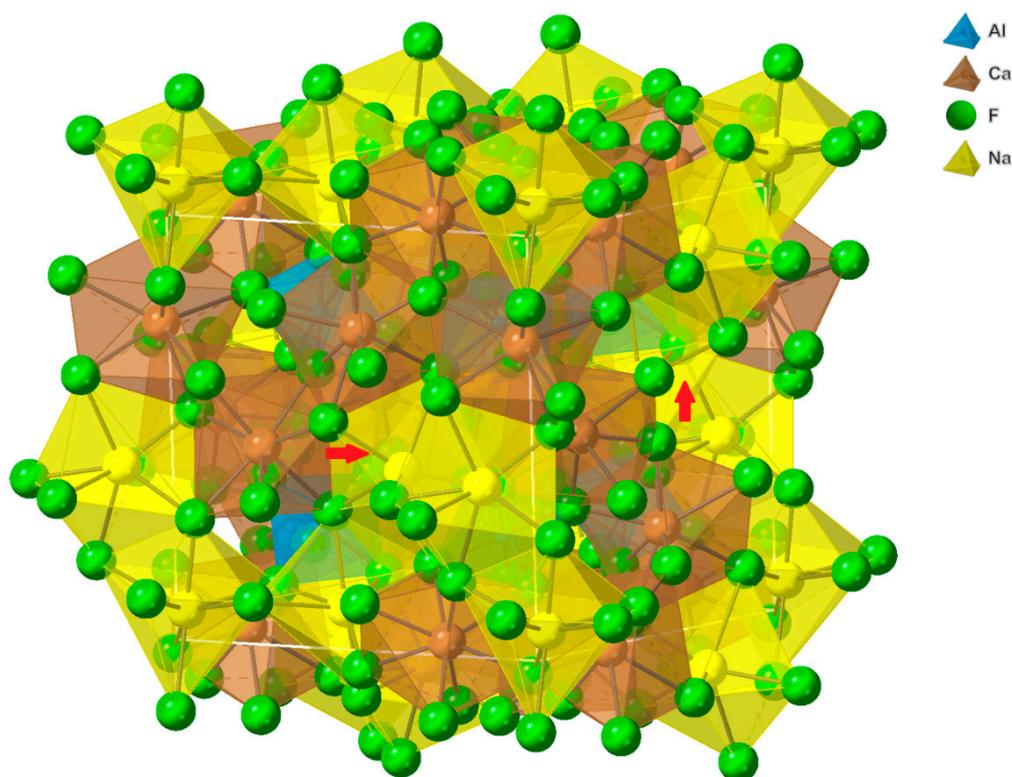


Figure 5. A general direction view of coordination polyhedra in one unit cell of verneite. Red arrows indicate the directions of sinuous chains of coordination polyhedra on the (100) and (010) surfaces of the unit cell. Projection based on crystal structure data from Reference [13].

4.2. NaF–CaF₂–AlF₃ System and the Natural Occurrences of Phases

Only three ternary phases have been originally reported in the phase system NaF–CaF₂–AlF₃ [32], the low-temperature form of NaCaAlF₆, its high-temperature polymorph, and NaCaAl₂F₉. Later investigations showed that the material investigated by Craig and Brown [32] and reported as the low-temperature form of NaCaAlF₆ actually has the composition Na₂Ca₃Al₂F₁₄ [13]. In addition, the composition of NaCaAl₂F₉ was corrected to the structural formula Na₄Ca₄Al₇F₃₃ [20]. NaCaAlF₆ was confirmed to have a high-temperature (stable above 620 °C) and a low-temperature form, based on determinations of their structures [20,24]. The crystal structure data for the four confirmed phases in the phase system are represented in Table 4. To the best of our knowledge, none of the phases from this phase system have been observed before in nature, and Na₂Ca₃Al₂F₁₄ reported here is the first example. The synthetic work showed that this compound is stable up to 719 °C at atmospheric pressure and decomposes at higher temperatures to a mixture of the high-temperature NaCaAlF₆ and fluorite [13]. It forms readily at temperatures lower than 600 °C in the part of the phase system comprising approximately equal molar amounts of Na, Ca, and Al, and it crystallizes rather than the low-temperature form of NaCaAlF₆, which is metastable and could be synthesized only through hydrothermal synthesis [20]. The fourth ternary phase in this phase system, Na₄Ca₄Al₇F₃₃, is reported to form through a sluggish reaction between Na₂Ca₃Al₂F₁₄ and AlF₃ [32]. The metastability of NaCaAlF₆ below 600 °C and the slow-forming reaction of Na₄Ca₄Al₇F₃₃ most probably explain the appearance of verneite as the only ternary Na–Ca–Al fluoride in fumaroles.

Table 4. Crystal structure data for the ternary phases from the NaF–CaF₂–AlF₃ system.

Formula	Space Group	Crystal lattice Parameters	Structure Type	Aluminofluoride Part	Ref.
β-NaCaAlF ₆	P321	8.9295(9), 5.0642(2) Å	Na ₂ SiF ₆	isolated [AlF ₆]	[20]
α-NaCaAlF ₆	P2 ₁ /c	8.7423(3), 5.1927(2), 20.3514(9) Å, 91.499(2)°	unique	isolated [AlF ₆]	[24]
Na ₂ Ca ₃ Al ₂ F ₁₄	I2 ₁ 3	10.257(1) Å	unique	isolated [AlF ₆] plus additional F	[13]
Na ₄ Ca ₄ Al ₇ F ₃₃	Im3m	10.781(3) Å	unique	[Al ₇ F ₃₃] 3D framework	[20]

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References

- Jakobsson, S.P.; Leonardsen, E.S.; Balić-Žunić, T.; Jónsson, S.S. Encrustations from three recent volcanic eruptions in Iceland: The 1963–1967 Surtsey, the 1973 Eldfell and the 1991 Hekla eruptions. *Fjölrít Náttúrufræðistofnunar* **2008**, *52*, 65.
- Balić-Žunić, T.; Garavelli, A.; Acquafredda, P.; Leonardsen, E.; Jakobsson, S.P. Eldfellite, NaFe(SO₄)₂, a new fumarolic mineral from Eldfell volcano, Iceland. *Mineral. Mag.* **2009**, *73*, 51–57. [[CrossRef](#)]
- Garavelli, A.; Balić-Žunić, T.; Mitolo, D.; Acquafredda, P.; Leonardsen, E.; Jakobsson, S.P. Heklaite, KNaSiF₆, a new fumarolic mineral from Hekla volcano, Iceland. *Mineral. Mag.* **2010**, *74*, 147–157. [[CrossRef](#)]
- Balić-Žunić, T.; Garavelli, A.; Mitolo, D.; Acquafredda, P.; Leonardsen, E. Jakobssonite, CaAlF₅, a new mineral from fumaroles at the Eldfell and Hekla volcanoes, Iceland. *Mineral. Mag.* **2012**, *76*, 751–760. [[CrossRef](#)]
- Mitolo, D.; Garavelli, A.; Balić-Žunić, T.; Acquafredda, P.; Jakobsson, S.P. Leonardsenite, MgAlF₅(H₂O)₂, a new mineral species from Eldfell volcano, Heimaey Island, Iceland. *Can. Mineral.* **2013**, *51*, 377–386. [[CrossRef](#)]
- Jacobsen, M.J.; Balić-Žunić, T.; Mitolo, D.; Katerinopoulou, A.; Garavelli, A.; Jakobsson, S.P. Oskarssonite, AlF₃, a new fumarolic mineral from Eldfell volcano, Heimaey, Iceland. *Mineral. Mag.* **2014**, *78*, 215–222. [[CrossRef](#)]
- Balić-Žunić, T.; Garavelli, A.; Mitolo, D. Topsøeite, FeF₃(H₂O)₃, a new fumarolic mineral from the Hekla volcano, Iceland. *Eur. J. Mineral.* **2018**, *30*, 841–848. [[CrossRef](#)]
- Balić-Žunić, T. (University of Copenhagen, Copenhagen, Denmark); Jonasson, K. (Icelandic Institute of Natural History, Gardabaer, Iceland). Personal communication, 2013.
- Ruste, J. X-Ray spectrometry. In *Microanalysis and Scanning Electron Microscopy*; Maurice, F., Meny, L., Tixier, R., Eds.; Les Editions de Physique: Orsay, France, 1979; pp. 215–267.
- Acquafredda, P.; Paglionico, A. SEM-EDS microanalyses of microphenocrysts of Mediterranean obsidians: A preliminary approach to source discrimination. *Eur. J. Mineral.* **2004**, *16*, 419–429. [[CrossRef](#)]
- Balić-Žunić, T.; Vicković, I. IVTON—Program for the Calculation of Geometrical Aspects of Crystal Structures and Some Crystal Chemical Applications. *J. Appl. Cryst.* **1996**, *29*, 305–306. [[CrossRef](#)]
- Mandarino, J.A. The Gladstone-Dale relationship. I. Derivation of new constants. *Can. Mineral.* **1976**, *14*, 498–502.
- Courbion, G.; Ferrey, G. Na₂Ca₃Al₂F₁₄: A new example of a structure with “independent F[−]”—A new method of comparison between fluorides and oxides of different formula. *J. Solid State Chem.* **1988**, *76*, 426–431. [[CrossRef](#)]
- Effenberger, H.; Kluger, F. Ralstonit: Ein Beitrag zur Kenntnis von Zusammensetzung und Kristallstruktur. *N. Jahrb. Miner. Monat.* **1984**, *1984*, 97–108.

15. Sawada, H. An electron density residual study of alpha-ferric oxide. *Mater. Res. Bull.* **1996**, *31*, 141–146. [[CrossRef](#)]
16. Balić Žunić, T.; Makovicky, E. Determination of the centroid or “the best centre” of a coordination polyhedron. *Acta Cryst.* **1996**, *B52*, 78–81. [[CrossRef](#)]
17. Makovicky, E.; Balić-Žunić, T. New measure of distortion for coordination polyhedra. *Acta Cryst.* **1998**, *B54*, 766–773. [[CrossRef](#)]
18. Balić-Žunić, T. Use of three-dimensional parameters in the analysis of crystal structures under compression. In *Pressure-Induced Phase Transitions*; Grzechnik, A., Ed.; Transworld Research Network: Kerala, India, 2007; pp. 157–184, ISBN 81-7895-272-6.
19. Bolotina, N.B.; Maximov, B.A.; Simonov, V.I.; Derzhavin, S.I.; Uvarova, T.V.; Apollonov, V.V. Crystal structure and spectral characteristics of LiCaAlF₆:Cr³⁺ single crystals. *Crystallogr. Rep.* **1993**, *38*, 446–450.
20. Hemon, A.; Courbion, G. The NaF-CaF₂-AlF₃ system: Structures of beta-NaCaAlF₆ and Na₄Ca₄Al₇F₃₃. *J. Solid State Chem.* **1990**, *84*, 153–164. [[CrossRef](#)]
21. Hemon, A.; Le Bail, A.; Courbion, G. Crystal structure approach of KCaAl₂F₉. A new hexagonal tungsten-bronze related structure. *Eur. J. Solid State Inor. Chem.* **1993**, *30*, 415–426. [[CrossRef](#)]
22. Hemon, A.; Courbion, G. Refinement of the room-temperature structure of alpha-CaAlF₅. *Acta Cryst. C* **1991**, *47*, 1302–1303. [[CrossRef](#)]
23. Domesle, R.; Hoppe, R. The crystal structure of Ca₂AlF₇. *Z. Kristallogr.* **1980**, *153*, 317–328. [[CrossRef](#)]
24. Le Bail, A.; Hemon-Ribaud, A.; Courbion, G. Structure of alpha-(Na Ca Al F₆) determined ab initio from conventional powder diffraction data. *Eur. J. Solid State Inor. Chem.* **1998**, *35*, 265–272. [[CrossRef](#)]
25. Werner, F.; Weil, M. Alpha-(BaCaAlF₇). *Acta Cryst. E* **2003**, *59*, 17–19. [[CrossRef](#)]
26. Litvin, A.L.; Petrunina, A.A.; Ostapenko, S.S.; Povarennykh, A.S. The crystal structure of usovite. *Dopov. Akad. Nauk Ukr. RSR Ser. B* **1980**, *3*, 47–80. (In Ukrainian)
27. Kampf, A.R.; Yang, H.; Downs, R.T.; Pinch, W.W. The crystal structures and Raman spectra of aravaipaite and calcioaravaipaite. *Am. Mineral.* **2011**, *96*, 402–407. [[CrossRef](#)]
28. Mumme, W.G.; Grey, I.E.; Birch, W.D.; Pring, A.; Bougerol, C.; Wilson, N.C. Coulsellite, CaNa₃AlMg₃F₁₄, a rhombohedral pyrochlore with 1:3 ordering in both A and B sites, from the Cleveland mine, Tasmania, Australia. *Am. Mineral.* **2010**, *95*, 736–740. [[CrossRef](#)]
29. Swanson, H.E.; Tatge, E. Standard X-ray diffraction powder patterns. *Nat. Bur. Stand. Circ.* **1953**, *539*, 69–70.
30. Bevan, D.J.M.; Straehle, J.; Greis, O. The crystal structure of tveitite, an ordered yttrifluorite mineral. *J. Solid State Chem.* **1982**, *44*, 75–81. [[CrossRef](#)]
31. The American Mineralogist Crystal Structure Database. Available online: <http://rruff.geo.arizona.edu/AMS/amcsd.php> (accessed on 28 November 2018).
32. Craig, D.F.; Brown, J.J. Phase equilibria in the system CaF₂-AlF₃-Na₃AlF₆ and part of the system CaF₂-AlF₃-Na₃AlF₆-Al₂O₃. *J. Am. Ceram. Soc.* **1977**, *63*, 254–261. [[CrossRef](#)]

