Aluminum fluoride hydrates, volcanogenic salts from Mount Erebus, Antarctica

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Abstract

Three aluminum fluoride hydrates, β-AlF$_3 \cdot$H$_2$O, AlF$_3 \cdot$3H$_2$O, and ralstonite (Na$_x$-Mg$_x$Al$_{2-x}$(F,OH)$_6 \cdot$H$_2$O) have been identified in volcanogenic incrustations from the summit area of Mount Erebus, Ross Island, Antarctica; anhydrous AlF$_3$ is probably also present. Associated salts are difficult to identify because of xrd-peak overlap, compositional variations, and, perhaps, postsampling changes in structural water.

The monohydrates and anhydrous AlF$_3$ coexist in sublimates crystallized directly from the Mount Erebus plume, whereas the trihydrate forms in aqueous solutions condensed from the volcanic plume, possibly by hydration of the monohydrates or AlF$_3$. Only AlF$_3 \cdot$3H$_2$O could be isolated for characterization. It occurs as euhedral cubes 1–6 μm on edge; unit-cell (tetragonal) dimensions are $a_0 = 7.726(1)$ Å and $c_0 = 3.657(1)$ Å; mean refractive index and calculated density are 1.413(1) and 2.09 g/cm^3, respectively.

Identification of aluminum trifluoride and its hydrates in volcanic incrustations suggests that AlF$_3$ is one of the principal high-temperature salts present in the plumes of Mount Erebus and many other volcanoes.

Introduction

Aluminum trifluoride (AlF$_3$) is thought to be one of the principal high-temperature volcanogenic salts that form incrustations by fractional condensation of volcanic gases (Oskarsson, 1981). Although AlF$_3$ has never been positively identified as a mineral, the gaseous molecule may be present as an initial constituent of the volcanic plume at Mount Hekla in Iceland (Oskarsson, 1981) and at many other volcanoes. Observation of AlF$_3$ as a sublimate in volcanic incrustations would serve to confirm this hypothesis.

Mount Erebus (elevation, 3794 m) is the most active volcano in Antarctica and the largest of four volcanic cones that form Ross Island. The predominant rock type on Mount Erebus and the only one cropping out in the summit area is anorthoclase phonolite (Giggenbach et al., 1973; Kyle et al., 1976). The active crater contains a small persistent lava lake of phonolitic magma. Fumarolic activity has been continuous at the summit since the discovery of Mount Erebus in 1841 (Jones et al., 1983).

Incrustations of salts are widely distributed along the coast of Ross Island and in the summit area. Many are yellowish in color and so resemble native sulfur, which has not been reported on Mount Erebus (Jones et al., 1983). These salts appear to have been deposited directly from the plume of volcanic gases and indirectly from it by interaction of the acid gases with volcanic rocks.

Mount Erebus is an ideal site for the study of F-bearing volcanic sublimates because it is an active, alkaline volcano and because unique conditions (low temperature, high altitude) exist at its summit. F-rich volcanic gases are associated with alkaline volcanoes (Stormer and Car-

michael, 1971). Furthermore, water-soluble sublimates destroyed or modified by hydrolysis at other volcanoes are more likely to be preserved at the summit of Mount Erebus.

A study of six small samples of incrustations from the summit area, acquired in 1979 through the kindness of William Zoller of the University of Maryland, was undertaken in an effort to establish the presence of AlF$_3$ and/or its hydrates.

Identification of phases

Positive identification of the crystalline phases in incrustations from the summit area is difficult because of their fine grain size and complex mineralogy. The presence of compositional variations and postsampling changes in structural water are further obstacles to mineral identification.

Attempts to fit observed X-ray patterns to those of known inorganic compounds have met with limited success (Jones et al. 1983). However, a list of crystalline phases positively or tentatively identified in samples from the summit area (Keys and Williams, 1981) includes various chlorides, sulfates, and fluorides; aluminum trifluoride (AlF$_3$) and ralstonite [Na$_x$Mg$_x$Al$_{2-x}$(F,OH)$_6 \cdot$H$_2$O] were tentatively identified by means of X-ray diffractometry.

X-ray diffraction data (Table 1) for qualitative analysis were collected using a monochromator-equipped diffractometer and Cu$K\alpha$ radiation. The goniometer was calibrated using several X-ray reflections from an external Si standard. Data were obtained by averaging two measurements per reflection at a scan rate of 1°/min. The preci-
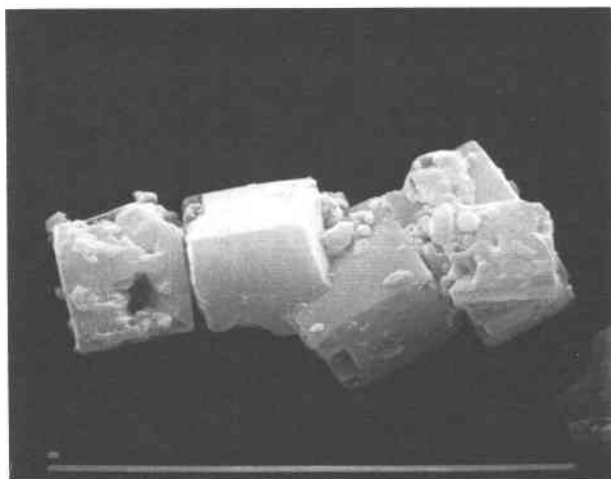
Fig. 1. Scanning-electron microphotograph of $AlF_3 \cdot 3H_2O$. The length of the bar is 18.3 μm.

TABLE 1. X-ray powder-diffraction data for salt sample E398 from the summit of Mount Erebus, Ross Island, Antarctica, and for synthetic $AlF_3 \cdot 3H_2O$

Salt sample		$AlF_3 \cdot 3H_2O$*		Salt sample		$AlF_3 \cdot 3H_2O$*	
d (Å)	I/I₀	d (Å)	I/I₀	d (Å)	I/I₀	d (Å)	I/I₀
9.646	5			2.870	5		
8.927	10			2.812	5		
7.609	3			2.728	20	2.73	30
6.794	3			2.649	15	2.65	9
5.901	5			2.612	5		
5.824	5			2.540	5		
5.741	5			2.506	20	2.51	12
5.453	100	5.45	100	2.440	30	2.44	55
4.897	8			2.366	5		
4.657	10			2.325	5		
4.436	10			2.302	5		
4.329	15			2.279	3		
4.267	20			2.187	10	2.19	5
4.055	5			2.102	5	2.11	2
3.864	50	3.86	60	2.050	10		
3.659	20	3.65	5	2.030	20	2.03	12
3.531	5			2.015	8		
3.504	5			1.930	10	1.933	13
3.477	5			1.847	10	1.850	8
3.398	20			1.819	8	1.824	7
3.336	35	3.33	17	1.794	10		
3.299	40			1.775	20	1.780	8
3.213	5			1.726	25	1.728	40
3.031	25	3.04	14	1.668	5	1.670	5
2.915	10						

* JCPDS card no. 9-108.

sion of these measurements is believed to be within 0.02° 2θ for all reflections and $\pm 0.01°$ 2θ for the stronger reflections.

Two mineralogically distinct sample groups were recognized by means of X-ray diffractometry. The X-ray powder-diffraction patterns of five samples in one group, represented by sample E68 (Table 4), are very similar to that reported for a salt sample from the summit area of Mount Erebus by Jones et al. (1983). The X-ray diffraction pattern of the remaining sample, E398 (Table 1), is unique. The location of sampling sites within the summit area is unknown.

Salt sample E398

Phases present. A search of the Joint Committee on Powder Diffraction Standards (JCPDS) listing of inorganic compounds using the three most intense X-ray diffraction maxima (Table 1) yielded an acceptable match with $AlF_3 \cdot 3H_2O$ [JCPDS card no. 9-108] based on the positions and relative intensities of 18 X-ray reflections. The trihydrate has not been reported in nature to date. The identity of the other phases composing the sample could not be established definitely because of the apparent overlap of X-ray reflections of several coexisting phases.

In an attempt to identify additional phases, semiquantitative analyses for Na, K, Ca, Al, Si, Fe, Mg, and S were carried out using the analytical electron microscope (AEM) in the scanning mode. Five compositional groups were recognized on the basis of 54 random analyses of mineral grains: (1) Al only (15 analyses), identified as $AlF_3 \cdot 3H_2O$ based on morphology (see Fig. 1). (2) Si only (7 analyses) attributed to some form of SiO_2. Several X-ray reflections consistent with the presence of quartz were observed, but owing to peak overlap, a positive identification cannot be made by X-ray diffractometry. (3) S and Ca (5 analyses), probably representing the presence of a small amount of gypsum. Three unambiguous X-ray reflections 7.61, 2.87,

and 2.07 Å (Table 1) correspond to gypsum, which has been positively identified in the salts from the summit area of Mount Erebus (Keys and Williams, 1981). (4) Na and Al predominant (15 analyses), possibly representing a chloride or fluoride. (5) Si and K with lesser amounts of Al and Na (7 analyses) indicating the presence of a silicate. The remaining five analyses show the presence of Si and Al with lesser amounts of Na, K, and Ca, but elemental percentages vary widely, suggesting that these analyses represent mixtures of the above groups.

Characterization of $AlF_3 \cdot 3H_2O$. Natural $AlF_3 \cdot 3H_2O$ was characterized by refined unit-cell dimensions as well as by chemical composition and optical properties. X-ray data are compared with those for synthetic $AlF_3 \cdot 3H_2O$ in Table 2. Partial chemical analyses were obtained using an electron microprobe (EMP).

$AlF_3 \cdot 3H_2O$ occurs as cubes 1–6 μm on edge (average ~4.5 μm) (Fig. 1) in yellowish, poorly crystalline to gel-like masses. Isotropic material of low refractive index (<1.40), yellowish needlelike crystals often in radiating masses, and small rounded crystals with high birefringence are also present in this sample. The mean refractive index of natural $AlF_3 \cdot 3H_2O$, 1.413(1), is identical to the measured value for synthetic material, 1.4130(6) (Ryss, 1956, p. 587); both have very low birefringence.

$AlF_3 \cdot 3H_2O$ was synthesized by Ehret and Frere (1945) who published Debye-Sherrer X-ray powder data for the stable form. Freeman (1956) obtained crystallographic data for $AlF_3 \cdot 3H_2O$ based on measurements made using an X-ray diffractometer. He was able to index the powder
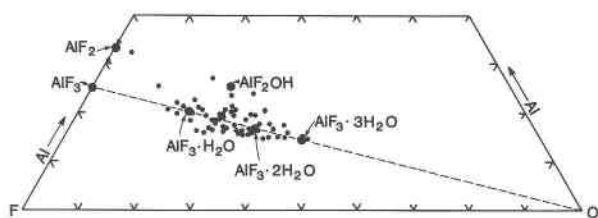
Fig. 2. Electron-microprobe analyses of $AlF_3 \cdot 3H_2O$ in the system Al-F-O. Compositions of hydrous aluminum fluorides have been projected into the anhydrous system. AlF_2 is a charged decomposition product.

TABLE 3. Partial chemical analysis of salt sample E68 (wt%)*

F	39.0
Na	10.3
Mg	0.43
Al	12.40
Si	1.9
S	0.81
Cl	19.5
K	0.43
Ca	0.21
Fe	1.29
Mn	0.35
Ti	0.06
	86.68

* W. H. Zoller, written comm., 1979.

pattern and calculate lattice parameters assuming a tetragonal unit cell. Although systematic absences were observed, it was not possible to define the space group unambiguously (Freeman, 1957). The density calculated on the basis of four formula weights per unit cell, 2.09 g/cm³, compares well with the measured density, 2.03 g/cm³, considering that no correction was made for solubility (Freeman, 1956).

X-ray data for natural $AlF_3 \cdot 3H_2O$ were recollected from the bulk sample at a scan rate of ½°/min; two data sets were averaged to obtain d values that are compared to those of Ehret and Frere (1945) and Freeman (1956) in Table 2. The d values and relative intensities are in excellent agreement particularly with the diffractometer data of Freeman (1956). The unit-cell dimensions of natural $AlF_3 \cdot 3H_2O$ calculated by least-squares refinement of 17 X-ray reflections are close to those reported for the synthetic end member (Table 2).

Partial chemical analyses were obtained using a Cameca Cambax electron microprobe. Because water loss

was anticipated, samples were mounted on a gold substrate using ethanol as a dispersant and analyzed at an accelerating potential of 8 kV. Al and F were the only elements detected; oxygen was determined by difference. The results are shown in Figure 2. Water has apparently been lost in almost every analysis; many analyses cluster around $AlF_3 \cdot 2H_2O$ and $AlF_3 \cdot H_2O$. HF has also been lost in analyses intermediate between $AlF_3 \cdot H_2O$ and AlF_2OH. A few analyses show complete loss of water as well as loss of HF and lie close to the composition AlF_2. These results are consistent with the identification of an aluminum fluoride hydrate and, together with the X-ray data, provide convincing evidence that its chemical formula is $AlF_3 \cdot 3H_2O$.

Salt sample E68

A partial chemical analysis (Table 3) by means of atomic absorption spectrophotometry and X-ray fluorescence

TABLE 2. X-ray powder-diffraction data for natural and synthetic $AlF_3 \cdot 3H_2O$

	Natural			Synthetic			
hkl	d_{obs} (Å)	d_{calc} (Å)	I/I_0	d_{obs} (Å)*	I/I_0	d_{obs} (Å)**	I/I_0
110	5.468	5.463	100	5.45	100	5.47	100
200	3.862	3.863	65	3.86	62	3.86	56
001	3.657	3.657	24	3.65	5	3.66	17
101	3.305	3.305	60	3.33	17	3.29	52
111	3.040	3.039	40	3.04	14	3.01	35
220	2.732	2.732	25	2.73	30	2.72	27
201	2.656	2.656	22	2.65	9	2.64	25
211	2.512	2.511	26	2.51	12	2.50	27
310	2.442	2.443	49	2.44	56	2.43	58
221	2.186	2.188	14	2.19	5	2.18	10
301	2.103	2.106	5	2.11	2	2.08	4
311	2.030	2.031	28	2.03	12	2.02	23
400	1.931	1.931	13	1.933	13	1.92	15
321	1.848	1.849	11	1.850	8	—	
{002} {330}	1.821	1.828	8	1.824	7	1.83	15
102	1.779	1.779	31	1.780	8	1.77	44
420	1.728	1.728	36	1.729	42	1.72	56
411	1.670	1.668	7	1.670	5	1.66	12
331	1.631	1.630	4	1.632	2		
212	1.616	1.616	7	1.618	2		
	$a = 7.726(1)$ Å				$a = 7.734$ Å		
	$c = 3.657(1)$ Å				$c = 3.665$ Å		

* Freeman (1956, 1957).
** Ehret and Frere (1945).

TABLE 4. X-ray powder-diffraction data for salt sample E68 from the summit of Mount Erebus, Ross Island, Antarctica, and for synthetic AlF_3, β-$AlF_3 \cdot H_2O$, $Al(OH)_{0.5}F_{2.5} \cdot H_2O$, and NaCl

E68		AlF_3*		β-$AlF_3 \cdot H_2O$*				$Al(OH)_{0.5}F_{2.5} \cdot H_2O$*				NaCl**	
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)†	I/I_0	d (Å)††	I/I_0	d (Å)‡	I/I_0	d (Å)‡‡	I/I_0	d (Å)	I/I_0
8.588	100												
7.596	9												
6.237	26			6.3	100	6.2	100						
5.717	6							5.72	100	5.70	100		
5.025	30												
4.541	26												
4.260	48												
3.797	3												
3.623	34			3.68	63	3.63	52						
3.517	45	3.52	100	3.58	27	3.55	24						
3.460	3									3.44	7		
3.249	3											3.258	13
3.220	6												
3.116	36			3.13 ⎫	79	3.11 ⎫	42						
3.069	7			3.08 ⎭		3.06 ⎭							
2.923	44							2.95	59	2.92	31		
2.831	11							2.83	31	2.80	29		
2.821	15											2.821	100
2.757	50												
2.550	14												
2.515	3	2.51	3	2.53	5	2.53	2						
2.473	9							2.45	8	2.43	3		
2.354	16			2.35	10								
2.332	8			2.32	4								
2.292	6					2.30	4						
2.268	3							2.27	7	2.22	3		
2.229	5					2.20	4						
2.128	24	2.119	20										
2.097	17												
2.061	13	2.074	3										
2.016	7	2.019	1	2.04	18	2.02	13						
1.994	20			2.03	16	1.932	13	1.99	21			1.994	50
1.981	15									1.98	28		
1.872	3							1.88	34	1.86	31		
1.802	6			1.817	32	1.798	20						
1.757	19	1.759	25	1.765	45	1.749	26						
1.722	3			1.742	8	1.726	4	1.73	34	1.71	25		
				1.691	10	1.682	6						
1.658	5												
1.643	2							1.65	9	1.63	14		
1.626	2											1.628	15
		1.600	3	1.614	6	1.598	3						
1.580	2	1.587	15	1.584	8	1.573	4						
1.558	3	1.560	7	1.560	16	1.545	10						
1.533	7							1.54	8	1.53	5		
1.520	4			1.529	22	1.515	11						
1.495	5							1.49	13	1.47	9		
1.462	10	1.460	1										

* Grobelny (1977).
** JCPDS card no. 5-0628.
† Synthesized at 140 °C.
†† Heated to 600 °C.
‡ Synthesized at 140 °C.
‡‡ Heated to 500 °C.

techniques was provided with this sample (Zoller, written comm., 1979). The analysis indicates that over 80 wt% of this sample consists of Na, Al, Cl, and F and that almost half of this percentage is F. Thus, the sample must contain largely chlorides and fluorides of Na and Al and the fluorides should predominate.

Comparison of X-ray diffraction maxima (Table 4) with those known for chlorides and fluorides strongly suggests the presence of β-$AlF_3 \cdot H_2O$ based on the position and relative intensities of 16 X-ray reflections. X-ray diffrac-

tion lines are listed (Table 4) for β-$AlF_3 \cdot H_2O$ synthesized from an AlF_3-bearing solution at 140 °C and for the same material after heating at 600 °C. Although the crystal structure is essentially unchanged, heating causes dehydration and contraction of cell parameters (Grobelny, 1977). The d spacings of β-$AlF_3 \cdot H_2O$ in the salt sample may be expected to lie within or close to the range of values for the fully and partially hydrated compounds (Table 4). The monohydrate has not been reported in nature to date. The presence of AlF_3 is suggested by six

reflections that also correspond to the monohydrate and three reflections unique to the anhydrous compound. Only two X-ray diffraction maxima of the monohydrate are missing in the salt sample, rather weak reflections at approximately 1.69 and 1.60 Å. The latter is the only reflection missing from the pattern for AlF_3.

Further examination of the X-ray diffraction pattern suggests that ralstonite may also be present in sample E68. Natural ralstonites ($Na_xMg_xAl_{2-x}(F,OH)_6 \cdot H_2O$) form an isostructural solid-solution series between basic aluminum fluoride hydrate ($x = 0$) and a Na- and Mg-rich end member ($x = 1$) (Pauly, 1965). Despite differences in chemical composition that include the F/OH ratio and the amount of water as well as the value of x in the structural formula, X-ray powder-diffraction patterns of members of this series differ very little (Pauly, 1965; Rosenberg, 1972; Grobelny, 1977). Thus, X-ray identification of ralstonite is not difficult but estimates of its chemical composition based on X-ray powder-diffraction data alone are not possible.

X-ray diffraction maxima for basic aluminum fluoride hydrate, $Al(OH)_{0.5}F_{2.5} \cdot H_2O$, precipitated from an AlF_3 solution at 140 °C and for the same material after dehydration at 500 °C are compared with those for the salt sample (Table 4). The d spacings of ralstonite in sample E68 should lie close to the range of values for hydrated and dehydrated basic aluminum fluoride. All twelve X-ray reflections for the basic aluminum fluoride have reasonable equivalents in the salt sample; at least 10 are unambiguous. Despite the low intensity of the 5.72-Å spacing in the salt sample as compared to the synthetic compound, presumably caused by preferred orientation, the presence of ralstonite is highly probable. Unfortunately, β-$AlF_3 \cdot H_2O$, AlF_3, and ralstonite could not be isolated for purposes of characterization.

Inasmuch as Al and F were accounted for, at least partially, the presence of Na-bearing chlorides was suspected. In fact, four of the five X-ray diffraction maxima for NaCl correspond closely to reflections in the diffractogram for sample E68 (Table 4) including 3.258 Å ($I/I_0 = 13$), 2.821 Å (100), 1.994 Å (55), and 1.628 Å (15); only the weak reflection at 1.701 Å (2) is missing in the salt sample. Thus, the presence of halite, NaCl, which has been positively identified in salt samples from the summit area (Keys and Williams, 1981), may be inferred.

The identity of other phases composing the sample could not be established with any degree of certainty based on X-ray diffraction data alone. Semiquantitative AEM analyses for Na, K, Ca, Al, Si, Fe, Mg, S, and Cl were carried out in an effort to identify additional phases. This study proved to be difficult because of the extremely fine grain size of the sample and because the AEM instrumentation available is capable of analysis only in the scanning mode. However, three compositional groups were recognized based on 48 random analyses of apparent mineral grains: (1) Al greatly predominant (65–80 normalized weight percent), attributed to aluminum fluorides; small amounts of Mg are associated with Al in some of these

analyses suggesting the presence of ralstonite. (2) Na, Al, and Cl with lesser amounts of Fe representing a chloride, possibly $NaAl_4O_4Cl_5$, which has been tentatively identified in salts from the summit area (Keys and Williams, 1981). Although the X-ray diffraction maxima of $NaAl_4O_4Cl_5$ are similar to many of the unassigned reflections in the salt sample, the correspondence is not exact, perhaps owing to the effects of solid solution. (3) Fe and S with lesser amounts of K, attributed to the presence of jarosite that has been tentatively identified in salts from the summit area (Keys and Williams, 1981). X-ray diffraction maxima of the salt sample do not confirm the presence of jarosite, which may occur in minor amounts. Si is virtually absent in all analyses.

MINERAL GENESIS

Although $AlF_3 \cdot 3H_2O$ is the only stable hydrate in temperature range 10–100 °C, higher hydrates (usually $AlF_3 \cdot 3.5H_2O$) precipitate from supersaturated solutions below 70 °C and gradually transform into $AlF_3 \cdot 3H_2O$; between 70 and 100 °C the stable trihydrate crystallizes directly from solution (Nielsen and Altintas, 1984). At higher temperatures lower hydrates are more stable than the trihydrate even in the presence of aqueous solutions at elevated pressures; β-$AlF_3 \cdot H_2O$ crystallizes directly from supersaturated AlF_3 solutions at temperatures above 115 °C usually along with $Al(OH,F)_3 \cdot H_2O$ (Grobelny, 1977). These hydrates lose water on heating and are eventually transformed into α-AlF_3, the most stable anhydrous form of AlF_3. However, β-AlF_3 and $Al(OH,F)_3$ persist to 640 and 550 °C, respectively.

Anhydrous AlF_3 and the monohydrates probably crystallized as sublimates directly from the volcanic plume. Incrustations containing these compounds are apparently common in the summit area of Mount Erebus. Keys and Williams (1981) report that AlF_3 has been tentatively identified in salts from the summit area. Furthermore an X-ray powder diffraction pattern of a sample from the summit area that is very similar to that of sample E68 (Table 4) has been published without any identification of constituent minerals (Jones et al., 1983).

On the other hand, $AlF_3 \cdot 3H_2O$ in salt sample E398 is not a sublimate crystallized directly from volcanic gas but a secondary product formed in aqueous solutions condensed partially or entirely from the vapor phase. $AlF_3 \cdot 3H_2O$ may have precipitated directly from solutions (Nielsen and Altintas, 1984; Sanjuan and Michard, 1987) condensed from volcanic gases or may have crystallized by transformation of higher hydrates that precipitated directly from these solutions (Nielsen and Altintas, 1984). Alternatively, AlF_3 or the lower hydrates, crystallized from the vapor phase, may have hydrated in solution at or below 100 °C to form the stable trihydrate. Inasmuch as AlF_3 has been tentatively identified in the salts from the summit area of Mount Erebus (Keys and Williams, 1981, and this study), hydration of AlF_3 seems to be the more likely mode of origin. The presence of silicates in salt

sample E398 suggests the reaction of acid gases or condensates with volcanic rock.

CONCLUSIONS

Three aluminum fluoride hydrates β-AlF$_3 \cdot$H$_2$O, AlF$_3 \cdot$3H$_2$O and ralstonite (Na$_x$Mg$_x$Al$_{2-x}$(F,OH)$_6 \cdot$H$_2$O) have been identified in volcanogenic incrustations from the summit area of Mount Erebus, Ross Island, Antarctica. β-AlF$_3 \cdot$H$_2$O and AlF$_3 \cdot$3H$_2$O are, heretofore, unreported in nature. Anhydrous AlF$_3$ is probably also present. Only the trihydrate could be isolated for characterization.

The monohydrates coexist with anhydrous AlF$_3$ in five samples that appear to represent assemblages of sublimates crystallized directly from the Mount Erebus plume. NaCl is also probably present, and NaAl$_4$O$_4$Cl$_5$ and KFe$_3^{3+}$(SO$_4$)$_2$(OH)$_6$, jarosite, are possible additional constituents.

The trihydrate that has been identified and characterized in a sixth sample from the summit area probably formed in aqueous solutions condensed from the volcanic plume, possibly by hydration of AlF$_3$ and/or the monohydrates. Quartz, gypsum, and a sodium-aluminum silicate are probably present in this sample, but many X-ray diffraction reflections remain unassigned.

AlF$_3$ with a sublimation temperature of 760 °C is one of the principal high-temperature salts inferred to exist in the volcanic plume of Mount Hekla, Iceland (Oskarsson, 1981). The identification of aluminum fluoride hydrates and probably anhydrous aluminum fluoride from the summit area of Mount Erebus confirms and extends previous tentative reports of their existence (Keys and Williams, 1981) and suggests that AlF$_3$ may be present along with many other species in the plumes of other volcanoes as hypothesized by Oskarsson (1981).

ACKNOWLEDGMENTS

REFERENCES CITED

Ehret, W.F., and Frere, F.J. (1945) Dimorphism in aluminum fluoride trihydrate. Journal of the American Chemical Society, 67, 64–68.

Freeman, R.D. (1956) Crystallographic evidence for the trihydrate of aluminum fluoride. Journal of Physical Chemistry, 60, 1152.

——— (1957) Crystallographic evidence for the trihydrate of aluminum fluoride. Journal of Physical Chemistry, 61, 256.

Giggenbach, W.F., Kyle, P.R., and Lyon, G.L. (1973) Present volcanic activity on Mount Erebus, Ross Island, Antarctica. Geology, 1, 135–136.

Grobelny, Marian. (1977) High temperature crystallization of aluminum fluoride. Course, hydrolysis, solid phases. Journal of Fluorine Chemistry, 9, 187–207.

Jones, L.M., Faure, Gunter, Taylor, K.S., and Corbato, C.E. (1983) The origin of salts on Mount Erebus and along the coast of Ross Island, Antarctica. Isotope Geoscience, 1, 57–64.

Keys, J.R., and Williams, Karen. (1981) Origin of crystalline, cold desert salts in the McMurdo region, Antarctica. Geochimica et Cosmochimica Acta, 45, 2299–2309.

Kyle, P.R., Giggenbach, W.F., and Keys, H.J.R. (1976) Volcanic activity of Mount Erebus, Ross Island. Antarctica Journal, 11, 270–271.

Nielsen, A.E., and Altintas, N.D. (1984) Growth and dissolution kinetics of aluminum fluoride trihydrate crystals. Journal of Crystal Growth, 69, 213–230.

Oskarsson, Niels. (1981) The chemistry of Icelandic lava incrustations and the latest stages of degassing. Journal of Volcanology and Geothermal Research, 10, 93–111.

Pauly, Hans. (1965) Ralstonite from Ivigtut, South Greenland. American Mineralogist, 50, 1851–1864.

Rosenberg, P.E. (1972) Compositional variations in synthetic topaz. American Mineralogist, 57, 169–187.

Ryss, I.G. (1956) The chemistry of fluorine and its inorganic compounds. Translation Series, U.S. Atomic Energy Commission, AEC-tr-3927, Oak Ridge, Tennessee (original in Russian).

Sanjuan, Bernard, and Michard, Gil. (1987) Aluminum hydroxide solubility in aqueous solutions containing fluoride ions at 50 °C. Geochimica et Cosmochimica Acta, 51, 1823–1831.

Stormer, J.C., Jr., and Carmichael, I.S.E. (1971) The free energy of sodalite and the behavior of chloride, fluoride and sulfate in silicate magmas. American Mineralogist, 56, 292–306.