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PARTICLE GEOCHEMISTRY OF VOLCANIC PLUMES OF ETNA AND MOUNT ST. HELENS

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Abstract. Particles in volcanic plumes include vapor condensates and reaction products of ash with vapors or condensed liquids, in addition to abundant silicate particles. In the 1980 Mount St. Helens plume we detected abundant (Na, K)Cl crystals as well as Ca sulfates, the latter commonly as overgrowths on ash or anthropogenic particles. Many of the chloride particles contained zinc and cadmium. High-temperature fumarolic incrustations showed strong enrichments of arsenic, zinc, alkalis, and iron. At Etna we did not detect chloride crystals but found abundant Al, Fe, and Ca sulfates. Sulfuric acid droplets were ubiquitous in both plumes. Bulk analyses of fumarole incrustations at Etna showed an enrichment in the rare earth elements (REE). The chemical and textural data of the plume particles indicate that chloride particles form relatively early and react later with sulfuric acid droplets to form sulfates. At Etna, aluminum as well as some REE are probably transported as volatile fluorine compounds. The differences in plume chemistry between Etna and Mount St. Helens are most likely related to differences in F/Cl ratios of the vapors. Based on the abundance of particulate chlorine in plumes, we suggest that only a small fraction of the total chlorine released during an eruption might reach the stratosphere in the vapor phase.

Introduction

Volcanic vapors provide a steady flow of elements from the earth's interior to the atmosphere and exocycle, most notably during explosive volcanic eruptions, but also continuously in passive vapor plumes. During high-temperature degassing from dome fissures and lava lakes, only limited condensation of vapors occurs on the vent walls, and most vapors escape as a hot plume into the atmosphere. Monitoring of such volatile fluxes may provide insight in the degassing of magmas and can be an aid in eruption forecasting [Rose et al., 1983]. The volcanogenic element fluxes provide a baseline for air pollution [e.g., Varekamp and Buseck, 1986].

In volcanic plumes, tiny particles form as a result of vapor condensation, reaction of vapors with air, or reaction of vapors or condensed liquids with silicate fragments [Oskarsson, 1980]. Ice cores from the polar regions contain a record of aerosol deposition; anomalously high concentrations of Zn, Cd, and S are usually attributed to periods of intense volcanic activity [e.g., Zoller et al., 1974; Boutron, 1980].

We studied the bulk trace-element chemistry of high-temperature fumarolic incrustations and single-particle chemistry in plumes of a basaltic and a calc-alkaline volcano to obtain a record of element transport in volcanic vapors. We collected plume particles and fumarolic incrustations at Mount St. Helens (United States) in August 1980 (3 months after the May 18 eruption) and during a less active period (July 1981). Etna (Italy) was sampled in 1981. In addition, vapors and fumarole incrustations were sampled at Colima volcano (Mexico), which was in a non-eruptive state during sampling in 1981. In this paper we present data on the chemistry and textural relations of single particles in plumes and on the bulk chemistry of fumarolic incrustations and discuss element transport in volcanic vapors.

Bulk chemical compositions of volcanic aerosols are given by Mroz and Zoller [1975], Phelan et al. [1982], Phelan-Kotra et al. [1983], Buat-Menard and Arnold [1978], and Vossler et al. [1981], for various volcanoes including Etna, Mount St. Helens, and El Chichon. Single-particle chemistry of particles from various volcanic plumes is discussed by Rose et al. [1980, 1982]. Work by Cadle [1973], Cadle and Blifford [1971], Cadle and Frank [1968], Cadle et al. [1967, 1969, 1979], and Cadle and Mroz [1978] on volcanic particles, and studies of leachates of freshly fallen ash [Rose, 1977; Taylor and Stoiber, 1973; Varekamp et al., 1984], indicate that sulfur tends to form sulfuric acid droplets and $CaSO_4$ overgrowths (further referred to as gypsum) on silicates. Rose et al. [1982] reported particle compositions for the 1980 Mount St. Helens plume including chlorides, sulfates, oxides, and fluorides of Ca, Na, K, Al, Mg, Zn, and Cu; their data suggest a shift in Cu/Zn ratios with time after the main eruption of 1980. The particle load of Colima's plume was dominated by sulfate particles [Casadevall et al., 1984]. Common trace elements in particles from volcanic plumes and high-temperature fumaroles are Zn, Cd, Au, Cu, Br, As, and Sb [Stoiber and Rose, 1974; Oskarsson, 1981; Phelan et al., 1982; Phelan-Kotra et al., 1983].

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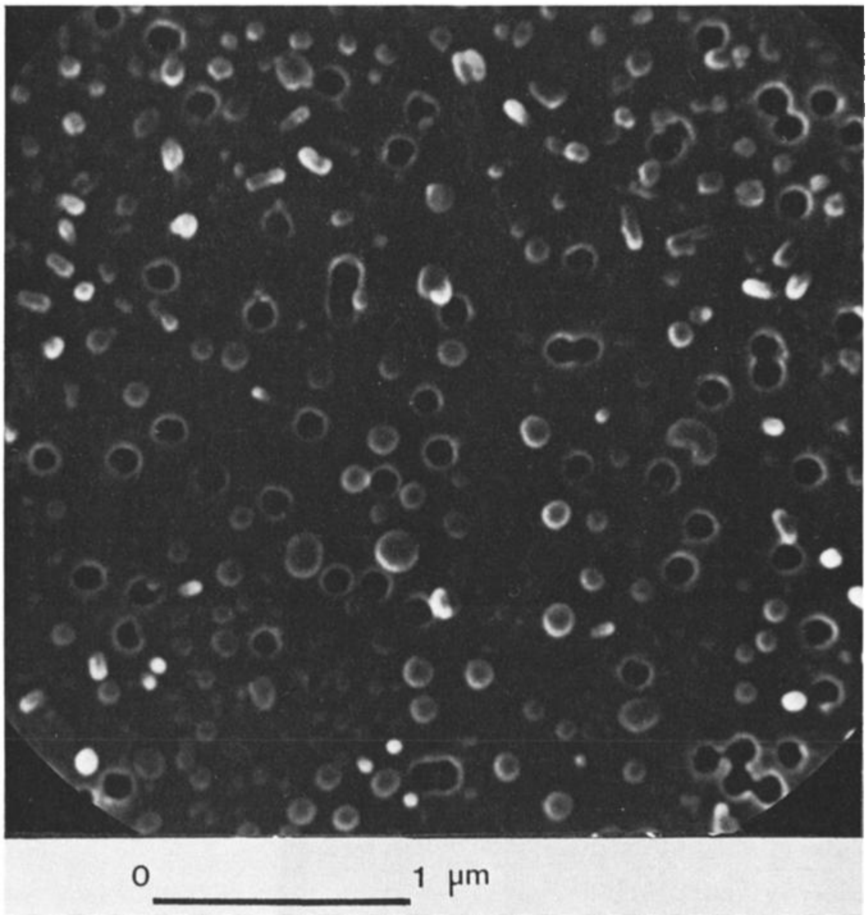

Fig. 1. Acid droplets on 0.2-μm filter, Mount St. Helens plume, 1980.

Methods and Techniques

Particles were collected from the Mount St. Helens plume during gas monitoring flights of the U.S. Geological Survey (USGS) in 1980 and 1981. A two-stage Nuclepore filter holder with filters with pore sizes 8 and 0.2 μm in diameter was fitted at the end of a 30-cm-long plexiglas tube and mounted on top of the aircraft wing. Collections were made at about 15 km downwind from the crater, at 2- to 3-km altitude, and at flying speeds of about 280 km/h in 1980, and at 2.5 km above the crater in a small, dilute plume in 1981. No opening or closing valves were used, so particles from outside the plume were also collected.

Fumarole incrustations from two small vents were sampled at Mount St. Helens in the south part of the crater in 1980. In 1981 the dome in the crater had grown considerably compared with 1980, and fumaroles had formed on cracks radially extending from the dome. Particles were collected at two sites (USGS location map codes: crack 109, 650°C and crack 107, 80°C) by pumping the gases through the two-stage Nuclepore filter holder described above. At Etna (1981) we sampled a fumarole in the southeast crater (420°C; the fumarole has disappeared after the 1985 eruptions), a 700°C fumarole in the northeast crater and the plume from the Bocca Nuova crater. Gases were pumped through the two-stage Nuclepore filter holder described above, and fumarolic incrustations were collected. At Colima volcano, incrustations were sampled from vents on the dome (420°C).

Vapors were also collected from all fumaroles for bulk trace element determination [Varekamp and Buseck, 1986], and bulk (particle + vapors) F-Cl-S contents. We employed gas-washing bottles with acid oxidizing solutions, which were analyzed by ion chromatography and instrumental neutron activation analysis (INAA).

The Nuclepore filters were cut in square sections of 5 x 5 mm, which were mounted on carbon planchets and coated with carbon for elemental analysis using an energy dispersive x-ray detector (EDS, PGT 2000) fitted on a Jeol JSM35 scanning electron microscope (SEM). A second set of filter squares was carbon-coated and subsequently coated with Au/Pd for imaging in the SEM. Micrographs were made at an accelerating voltage of 25 kV and at a sample current of about 1.5×10^{-11} A. Elemental analyses were obtained at an accelerating voltage of 15 kV and a sample current of about 4×10^{-10} A. A modified ZAF procedure was used for quantitative analysis of particles in the size range of 0.2 to 25 μm [Aden and Buseck, 1979; Aden, 1981]. We made additional semi-quantitative analyses at 25 kV to check for the presence of heavy elements (e.g., Hg and Pb). At 15 kV, F cannot be analyzed quantitatively on our system, but F peaks are present in the EDS spectra if this element is relatively abundant.

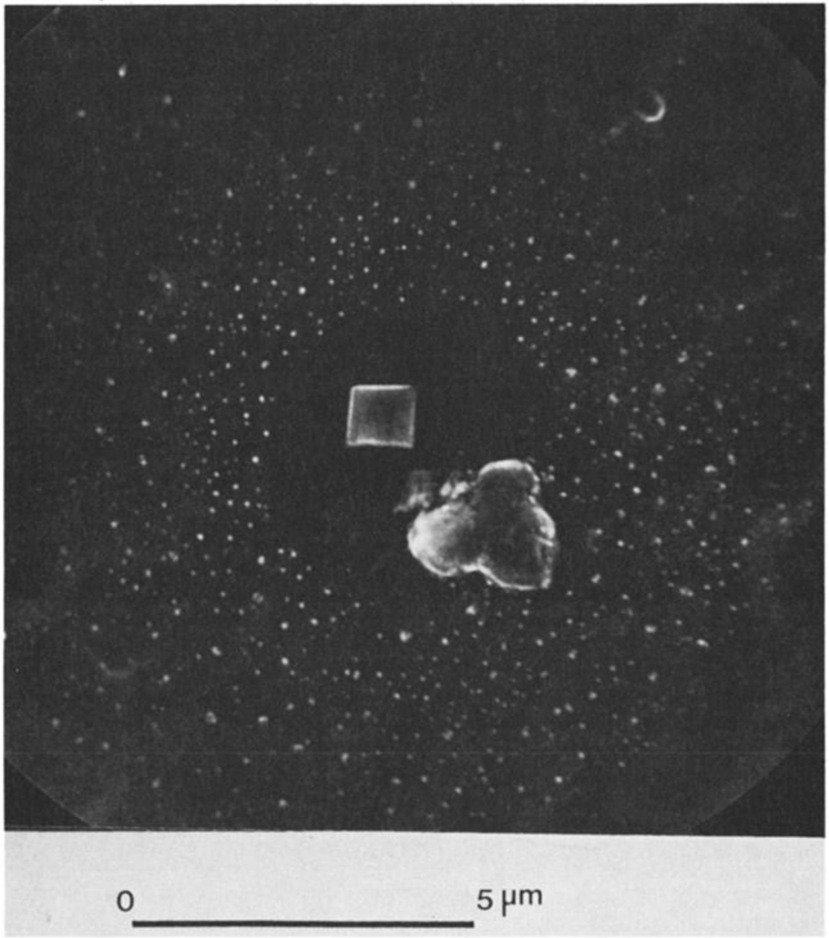

Fig. 2. Acid droplets in satellite rings around a cubic particle of (Na, K)Cl and spheroid particles of (Na, Ca) sulfates. Mount St. Helens plume, 1980.

Trace elements in the fumarolic incrustations were analyzed by INAA at Arizona State University.

Particle Studies

Mount St. Helens - 1980 Sample Set

Particles from the Mount St. Helens plume were present dominantly on the 8-μm pore size filter. Excluding silicate particles, we detected in order of abundance, acid droplets, condensate salts, and anthropogenic particles (Tables 1 and 2). Acidic droplets (Figure 1) showed only a S peak in their EDS spectrum, and the Nuclepore filters were commonly damaged around the droplets [see also Klockow et al., 1979]. These droplets are probably H_2SO_4. Submicron-sized particles that showed only a S peak in the EDS spectra disintegrated under the electron beam and are interpreted as ammonium sulfate that probably formed from H_2SO_4 on the filter [Klockow et al., 1979; Thomas and Buseck, 1983]. Droplets that showed only a Cl peak were rare. Many acidic droplets occurred as satellite rings around other particles (Figure 2) and formed when acid-enveloped particles impacted on the filter.

A second group of particles were cubes, spheroids, and overgrowths that contained S and/or Cl in combination with Na, K, Ca, and Mg (Figures 3, 4, 5, and Table 2). The cubes were usually between 0.5 and 3 μm in size and consisted of (Na, K)Cl, with minor amounts of S, Ca, and Mg. The spheroids contained mainly S, Na, and Ca, with minor Mg and K. The S/cation ratios suggest a stoichiometry of Na_2SO_4 and $CaSO_4$. Excess sulfur may occur as sulfuric acid, whereas cation excess (rare) probably results from the presence of anions undetected by EDS (e.g., nitrates and borates). Droplets of sulfuric acid were much more abundant than Cl-rich droplets, but solid salt particles were more commonly Cl-rich than S-rich. Many chloride cubes contained some Zn, Cd, Fe, and Cu; the sulfates contained Fe as the dominant metal. Chloride cubes tended to be corroded and overgrown by sulfate (Figures 4 and 5). Some chloride and sulfate salts formed crusts on anthropogenic particles, e.g., fertilizer grains (containing K, P, S, and Cl; McCrone and Delly [1973]) and hollow Cr-rich spheres (Figure 6; Cooper and Watson [1980]). The size of overgrowing salts was unrelated to the size of the host silicate particle. Some host particles lacking Ca and Na contained overgrowths rich in those elements.

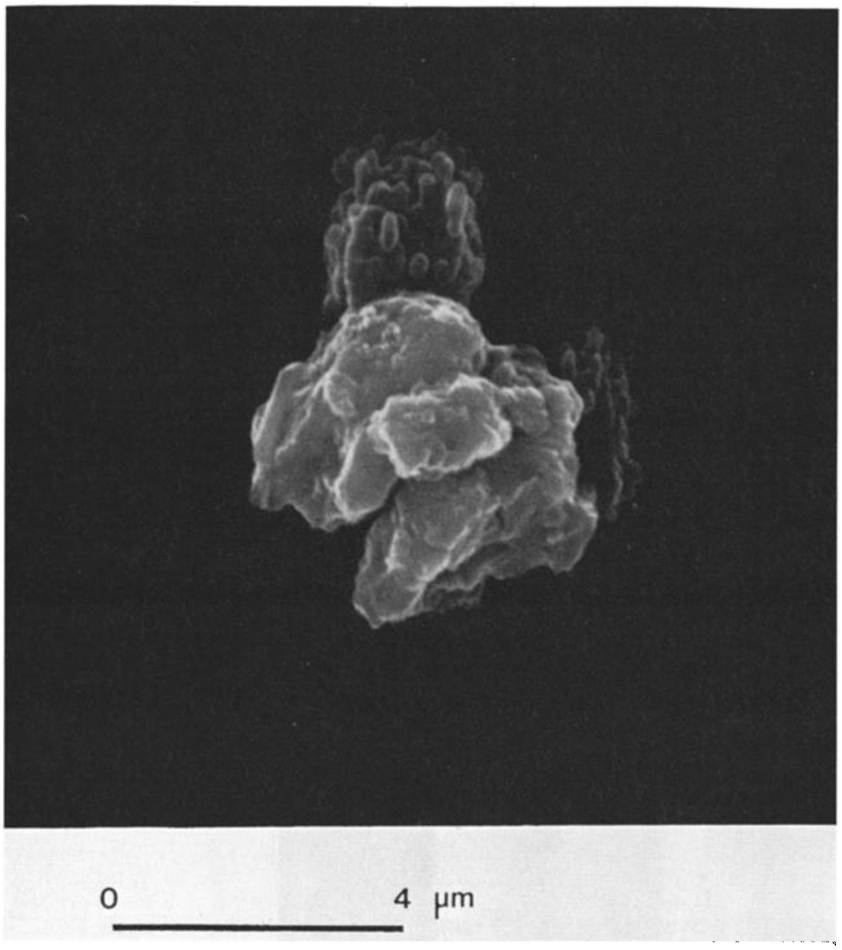

Fig. 3. (Na, Ca)SO_4 irregular particle overgrowing a silicate particle, Mount St. Helens plume, 1980.

Mount St. Helens - 1981 Sample Set

Acid droplets and ammonium sulfate particles were much less abundant in samples from the Mount St. Helens plume in 1981 than in 1980, and Cl-rich droplets were not detected in 1981. Condensate salts were less abundant but similar in composition to the salts detected in 1980 (Tables 1 and 2). Particle samples from a hot fumarole (650°C) contained abundant acid droplets, largely H_2SO_4 (Figure 7); Cl was not detected in droplets. The condensate salts were similar to those detected in the plume in 1980 and consisted generally of (Na, K) chlorides and (Na, Ca, and Mg) sulfates, with minor Cu, Zn, and Fe. Phases with Al and Fe as dominant cations occurred, probably partly Fe-oxides. A few overgrowths of silicate grains contained Pb, S, Fe, and Zn, or Hg, Cu, Fe, and S.

Particles from a low-temperature vent (80°C) contained gypsum (with minor Na and Fe) as overgrowths on silicates and sulfur-rich droplets but no chlorides.

Etna

Particles collected at Etna in fumaroles and in the Bocca Nuova plume (Tables 1 and 3) showed differences with the Mount St. Helens particles. Sulfuric acid droplets and ammonium sulfate particles (less than 0.2 μm in size) were abundant in samples from Etna's plume but less so in the two fumaroles (420°C and 700°C). No Cl-rich droplets were observed. Silicate particles were commonly overgrown with sulfates, as shapeless crusts and euhedral crystals (Figures 8 and 9).

Sulfate particles and overgrowths consisted of gypsum and Al and Fe sulfates, the former common in the fumaroles, the latter two in the plume (Figures 10 and 11). Sodium sulfate is rare. Copper and Zn occur in most sulfates, Ti is generally present in Fe sulfate, and Fe in gypsum and Al sulfate. Again, no relation exists between volume of the overgrowths and volume of the host particle, suggesting that the silicate cores of the particles were not the dominant source of elements for the overgrowths. One group of plume particles was rich in Al and S, and these showed a F-peak in the EDS spectra, and minor amounts of Cd. A damaged area in the filter around such Al sulfates (Figure 12) also contained F. We interpret these particles as Al sulfates covered with HF.

Fumarolic Incrustations and Vapors

X-ray diffraction analyses of the fumarolic incrustations showed the presence of gypsum and halite in the 1980 Mount St. Helens vent

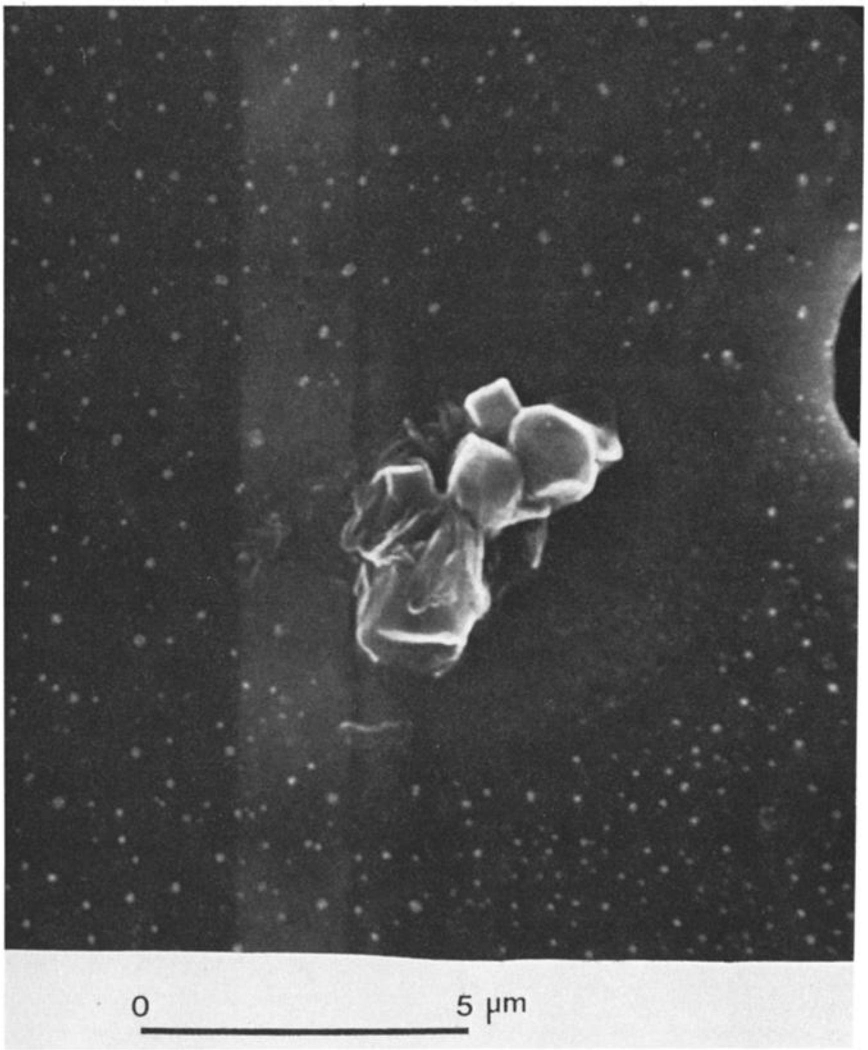

Fig. 4. Cubic chloride particles, partially corroded and overgrown by sulfate salts, Mount St. Helens plume, 1980.

deposits. Gypsum was the dominant deposit of the Etna fumaroles with a temperature between 150° and 250°C, whereas Al sulfate was detected at the 420° and 700°C vents. The 420°C vents at Colima carried exclusively Al sulfate, whereas the lower temperature vents had abundant gypsum. The amount of pure material did not permit an exhaustive study to detect any of the exotic minerals commonly found in fumarolic deposits [Stoiber and Rose, 1974].

Semi-quantitative energy-dispersive X-ray analyses of incrustations from the 1980 fumaroles at Mount St. Helens indicated enrichments in Cl and Br. The most Br-rich samples also contained abundant Ca and Na, with Zn, Cu, Pb, and Tl as most abundant trace elements (Figure 13).

Analyses by INAA of fumarole incrustations sampled in 1980 at Mount St. Helens and in 1981 at Etna and Colima volcano are shown in Table 4, together with analyses of representative rocks from these volcanoes. Alkalis, Zn, As, and Co were enriched in the Mount St. Helens samples (Cu cannot be detected by INAA). Analyses of gypsum incrustations from Etna show high rare earth element (REE) contents but no metal enrichments. The stalactitic growths of $Al_2(SO_4)_3$ on Colima volcano contained traces of As, Fe, Na, Se, and Zn.

Analyses of the fluids from gas-washing bottles yielded F/Cl (weight) ratios (Table 5), but most trace elements were below detection. We assume that the scatter in F/Cl ratios in fumes from one volcano and the lack of trace elements in solution are caused by adsorption of particles on the tubing walls of the collection apparatus.

Discussion

Important differences as well as similarities in particle chemistry exist between the plumes of Mount St. Helens and Etna (Table 1). The abundant sulfuric acid droplets result from oxidation of SO_2 [Cadle et al., 1971; Rose et al., 1980] and are typical for most volcanic plumes. The presence of (Na, K)Cl crystals indicates vapor transport of alkali chlorides with subsequent condensation of such chloride compounds. The 1981 Mount St. Helens plume carried much fewer chloride particles than the 1980 plume, probably related to the low Cl contents of the magma batches emplaced at Mount St. Helens after the May 18, 1980, eruption

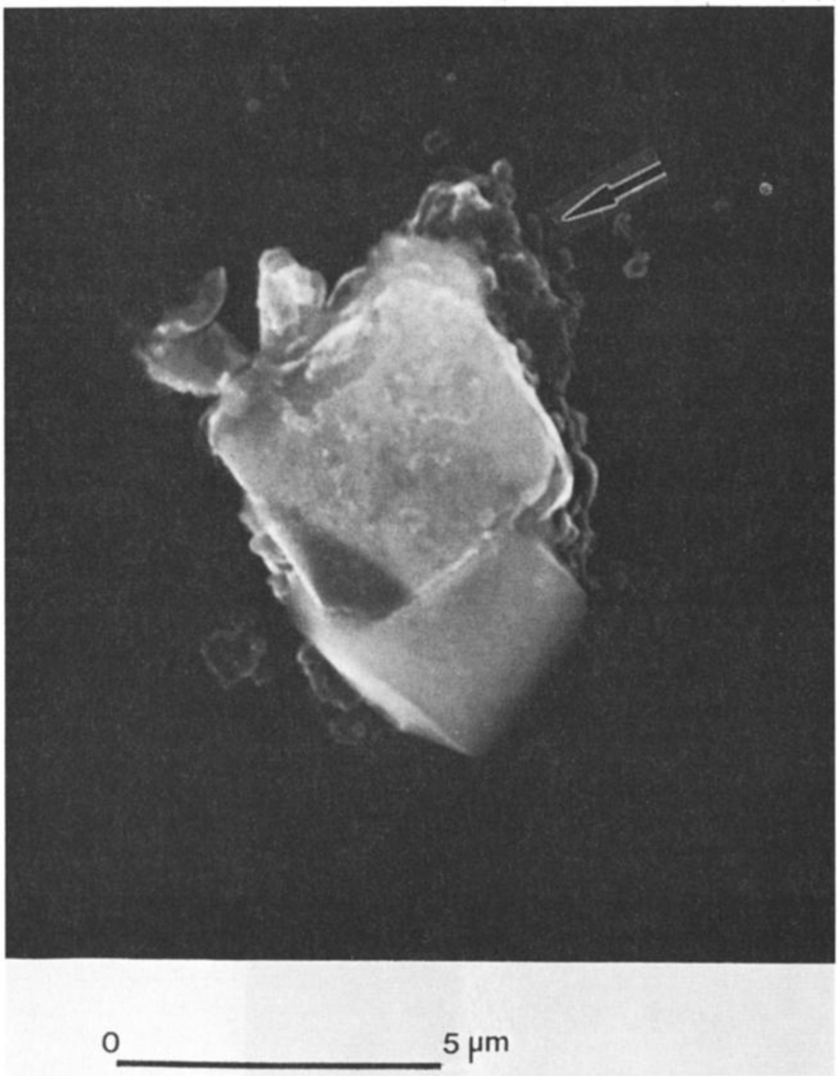

Fig. 5. Irregular sulfate crusts (arrow) on cubic chloride particles, Mount St. Helens plume, 1980.

TABLE 1. Particle Abundances in Plumes and Fumaroles; Etna, Mount St. Helens

	Etna		Mount St. Helens			
	Plume	Fumaroles	Plume		Fumaroles-1981	
		420°C	1980	1981	650°C	100°C
H_2SO_4 drops	xx	x	xx	x	xx	x
Cl-rich drops	o	o	x	o	o	o
Al sulfate	xx	xx	o	o	x	o
Fe sulfate	xx	xx	o	o	o	o
Ca sulfate	xx	xx	xx	*	x	xx
Na sulfate	x	x	xx	*	x	x
(Na, K)Cl	o	o	xx	*	*	o
AlF_3?	x	o	o	o	o	o
Fe - oxides	x	o	o	o	x	o

xx, abundant; x, common; o, absent; and *, rare.

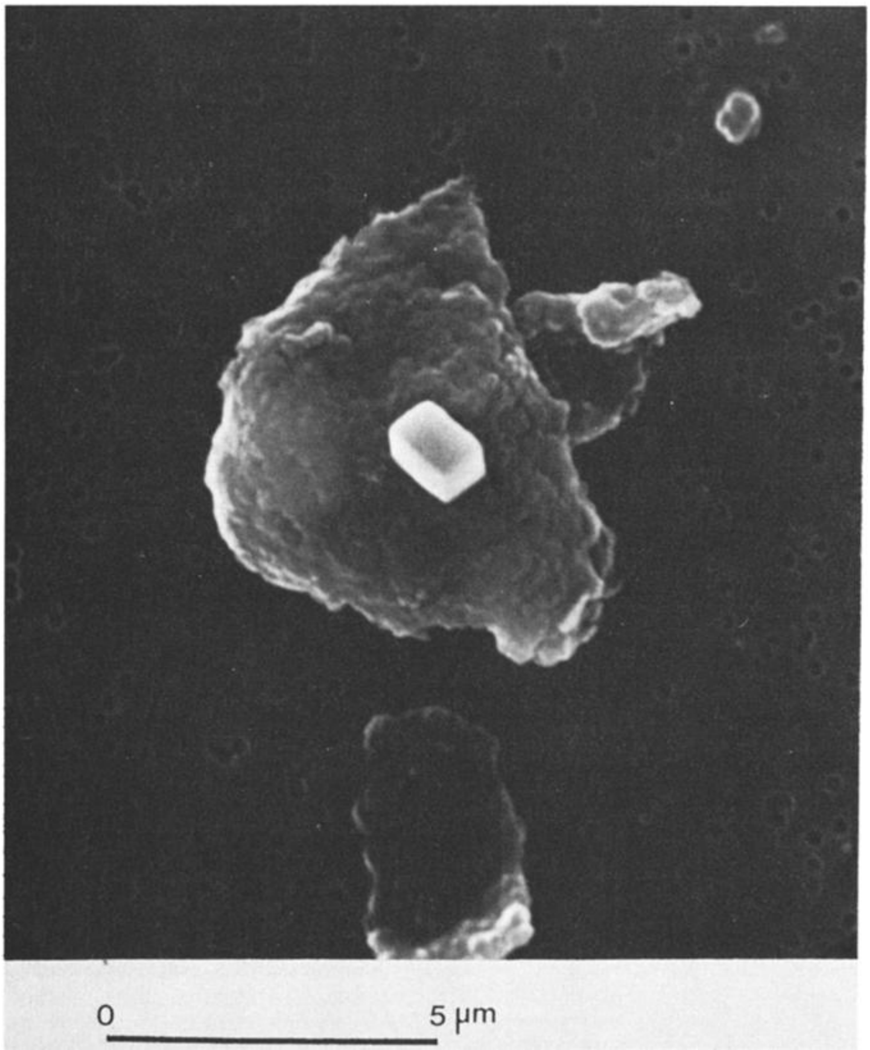

Fig. 6. Cubic (Na, K)Cl particle overgrowing hollow fragment of Cr-rich spheroid, Mount St. Helens plume, 1980.

[Rose et al., 1983]. Textural relations in the particles (e.g., Figure 5) suggest a relatively early condensation of the chlorides. Several analyses of (Na, K)Cl particles (Table 2) were made on single cubic crystals, suggesting initial precipitation as a single, homogenous phase. The system NaCl-KCl has a solvus with a crest at 500°C at 75 mol% NaCl [Levin et al., 1964]. Our analyses show maximum contents of 29 mol% KCl; probably such particles formed at temperatures of 500°C or more. Our analytical technique cannot establish whether later exsolution has occurred.

Chlorine occurs largely in solid particles. Rare Cl-rich droplets were found in the Mount St. Helens plume (1980) but not in the fumarole samples. Water condensation with subsequent absorption of HCl vapor may cause the formation of such droplets; these processes occur in the distal part of the volcanic plume only.

Visual observations of the SEM micrographs indicate the presence of Na sulfate and Ca sulfate crystals with a volume in excess of host silicate particles, which suggests vapor transport of at least part of the Ca and Na. Some Ca sulfate particles were found overgrowing on Ca-free hosts, also suggesting Ca transport in the vapor phase. Part of the Ca in sulfate particles, however, may have been derived from leaching of the host by sulfuric acid [Rose, 1977].

The presence of Al sulfates as particles and as stalactites in fumarolic vents suggests vapor transport of Al. The association of F with many Al sulfate particles, the "splashes" of F-bearing material on the filters, and the high F contents of the Colima fumaroles (with abundant Al sulfates) suggest a genesis according to the reaction

$$2AlF_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6HF$$

A similar reaction may occur in the plume of Erebus (Antarctica) because Al salts are abundant on its slopes [Keys, 1980, fide Rose et al., 1982] and its plume is also F-rich (M. Germani, unpublished results, 1985). Enrichment factors for volatile elements based on Al normalization (as used in many aerosol studies) might lead to erroneous conclusions in ash-poor and F-rich plumes.

Many particles from volcanic plumes bear evidence of a multiphase history: overgrowths, reaction rims, and corrosion are common. In

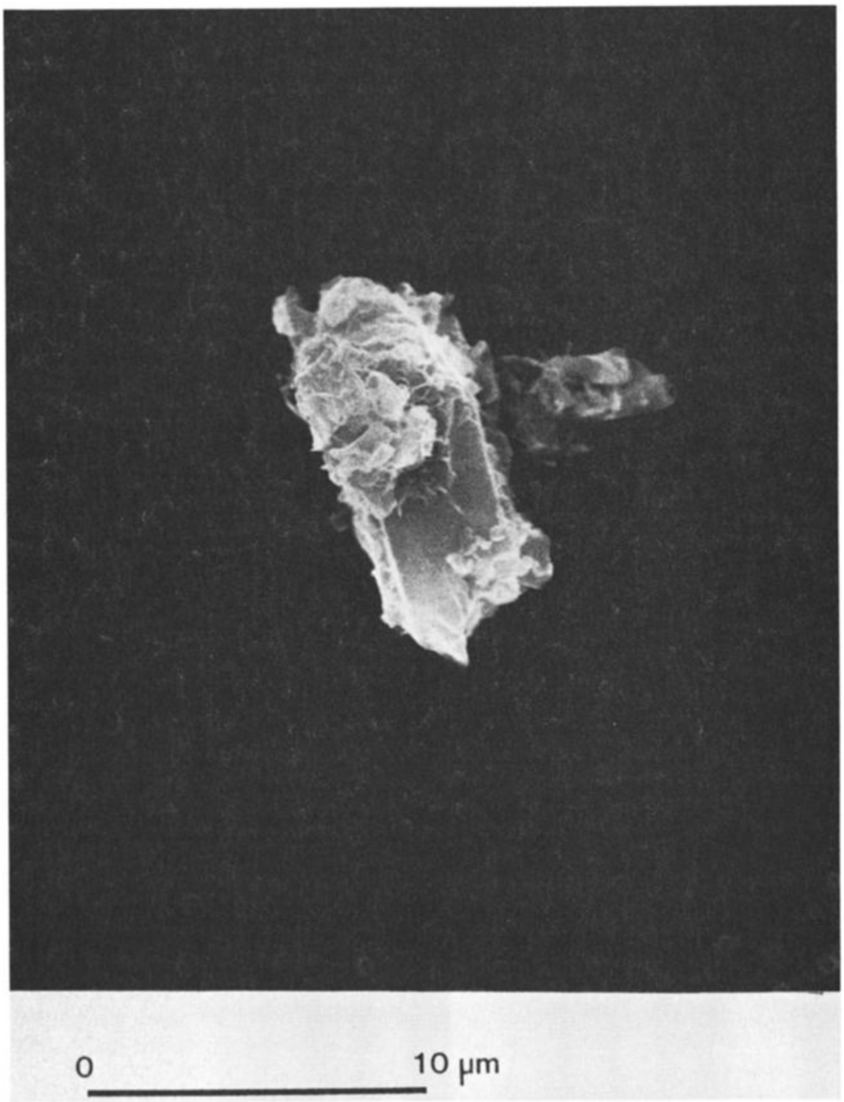

Fig. 7. Silicate particle with some sulfate overgrowths surrounded by abundant acid droplets, 650°C fumarole, Mount St. Helens, 1981.

fumaroles, incrustations with a spatial arrangement of different mineral assemblages can be related to cooling and increasing oxygen fugacities [Stoiber and Rose, 1974; Oskarsson, 1981]. In plumes, cooling and a continuously changing chemical environment impose constraints on the stability of mineral phases in the particles, and various minerals are found as overgrowths on each other. The common overgrowth of sulfates on chloride particles (Figure 5) as found at Mount St. Helens is probably a result of reaction between the earlier formed (Na, K)Cl particles and sulfuric acid. Presence of such overgrowths indicates that the plume has matured compared with freshly emitted vapors.

Vapor transport of Zn, Cd, and Fe is common at Mount St. Helens, as suggested earlier by Thomas et al. [1982] and Rose et al. [1982], and in agreement with Vossler et al. [1981] and Phelan et al. [1982], who also report strong enrichments in Zn and Cd in plume material from Mount St. Helens. Vapor transport of these metals is apparently less intense at Etna than at Mount St. Helens, which becomes particularly obvious when we compare the Zn flux for Etna (100 kg Zn/d with a SO_2 flux of 2000 t/d [Buat-Menard and Arnold, 1978] with that of Mount St. Helens (1000 kg Zn/d at 900 t SO_2/d, [Phelan et al., 1982]).

We calculated enrichment factors (EF's) with respect to presumed parent rocks for trace elements in fumarolic incrustations (Table 6). We used a Sc normalization procedure because Sc does not partition into the vapor phase and can be detected accurately by INAA. For example, the EF for cobalt in a sample is calculated as Co-sample/Co-parent rock multiplied by Sc-parent rock/Sc-sample. The Mount St. Helens sample shows a high EF for As, Rb and Cs and an extremely high EF for Zn. For Etna, EF's were calculated with respect to etnaite (the most common alkali basalt on Etna) as well as with respect to a trachyte, which possibly represents the composition of the glassy groundmass of the etnaites.

The high REE content of the gypsum-bearing samples of Etna is remarkable but comparable with the REE contents of anhydrite from El Chichon [Luhr et al., 1984]. The REE Ce and Eu are enriched most notably with respect to the

TABLE 2. Composition (in weight percent) of Selected Particles From Plume and Fumaroles, Mount St. Helens, 1980, 1981, as determined by SEM/EDS

D.#	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	MnO	TiO_2	Fe_2O_3*	SO_3	Cl_2	CuO	ZnO	CdO	P_2O_5
Plume 1980															
1		31.8	12.2		18.1					36.4					
4	2.1	20.0	11.4	1.8					0.4	2.9	45.3	10.2	5.8		
2	3.0	36.0	7.9	0.7					0.4	1.8	49.3		0.6		
7	8.3	16.8	14.8	3.9		1.7		2.0	3.2	10.4	33.9	1.4	1.5	1.5	
1	10.0	34.3			3.3						37.2			15.1	
15	12.6	23.1	7.2	12.5		3.1		0.6	2.5	6.1	31.3				1.3
2	22.5	16.0	13.1	2.5	1.6	10.5		0.9	3.2	2.8	23.7			2.3	
1	30.6	7.4	1.6	1.4		6.3			3.2	49.1					
Plume 1981															
3	8.5	24.4	11.3							10.3	41.9				
1		7.6	4.0	29.9						58.5					
9		43.8	0.6							54.2	1.4				
Fumarole 650°C, 1981															
21	44.3	13.9	7.1	3.7	1.4	6.6				9.5	13.5				
5	6.3	14.9	9.3	3.5		14.4			3.1	20.5	28.0				
3	15.8	3.4	7.8	2.1		35.8			3.5	32.3					
2	15.5	8.5	13.2			8.3			12.9	20.8	20.8				
7		9.4		18.1						55.2	14.5				
1	1.8								86.2	7.4	0.7	1.7	2.1		
1									86.9	11.3	1.8				
2	56.1	5.8	0.8	8.4	0.5	23.4			1.1	2.7		0.7	0.4		
2	21.7			30.5	0.4		0.5		15.1	31.8					

All values normalized to 100%.
D.: diameter, (μm)
* total Fe as Fe_2O_3.

TABLE 3. Composition (in weight percent) of Selected Particles From Plume and Fumaroles, Etna, as determined by SEM/EDS

D.#	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	TiO_2	MnO	Fe_2O_3*	SO_3	Cl_2	CuO	ZnO	CdO	P_2O_5
Fumarole 420°C															
4				40.6					0.6	58.8					
2						29.4			3.0	67.7					
1			1.5			13.6			10.4	73.8		0.7			
3	22.4	12.7	1.7	9.0	15.6	8.3	0.7	0.4	9.7	12.3	7.2				
1	28.2	3.6	1.5	3.4	0.7	16.9	0.8		5.5	38.9		0.2	0.3		
Fumarole 700°C															
1			1.1						31.3	66.8		0.8			
12						27.2				72.8					
9				4.4		17.9				76.2		0.6	0.8		
2				28.5			5.7		1.4	60.3		1.3	2.8		
3	41.9			6.1		1.6	3.4		18.3	28.1			0.6		
24	43.7		0.2	16.3					2.4	28.1		0.4	0.4		
Bocca Nuova Plume															
9				41.0						58.5		0.2	0.3		
1	1.1	1.7	1.6	34.0					1.9	59.6					
1	2.9	3.2	1.4	0.3	3.5	3.7	8.3	0.4	66.8	9.4					
1	5.1	3.7	0.7		10.0	5.0		0.3	11.8	62.0		0.5	0.9		
2[a]	11.8	18.4	3.3	9.3		46.1	0.3		3.8	6.1	0.3			0.5	
5	20.5	16.7	1.2	4.0	0.7	22.3			4.3	29.4					0.9
6	20.5	6.8	2.2	13.1		36.3			6.7	13.5	0.9				

All values normalized to 100%.
D.: diameter, (μm)
* total Fe as Fe_2O_3.
[a]: particle contains F, excluded from calculated analysis.

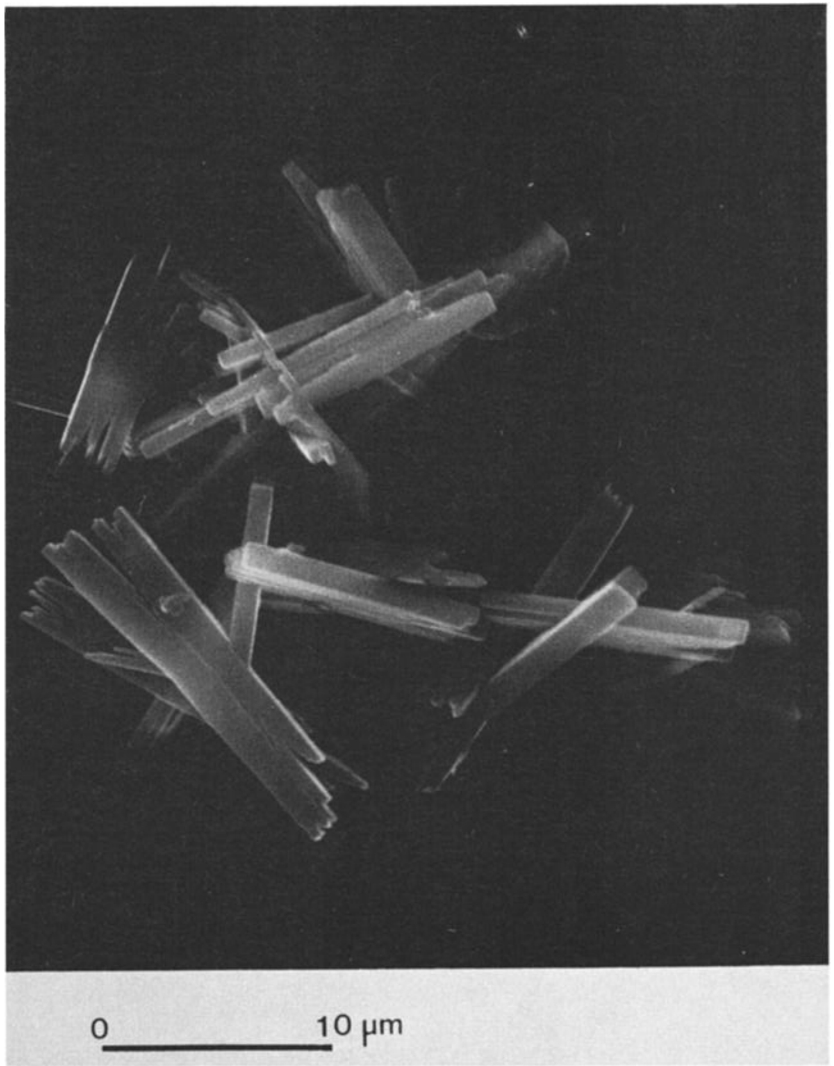

Fig. 8. $CaSO_4$ crystals, 700°C fumarole, Etna.

TABLE 4. Trace Element Data From Fumarolic Encrustations

	ETF2	ETF4	ETF6	Trach	Etn	CV3	CV6	SH30	SHA
Na. %	0.11	0.67	1.17			2.32	2.93	3.6	3.8
Fe. %	0.16	1.20	3.99			7.05	2.73	4.50	2.8
As ppm	2.7	3.1				4.7	33.8	349	2.8
Cr		6.9	8.8	40	185	76	38.5		
Co	1.0	5.3	17.4	27	44	23		15.3	9.4
Zn						132		9610	53
Hf	1.2	1.4	4.5	6.1	5.4	0.5		3.4	4.3
Sc	7.6	9.5	7.7	11.0	22.0	13.2	7.1	9.6	8.3
Th	6.2	6.7	1.8	16	14			3.1	3.3
U								1.1	1.2
Br	6.8	15.7				4.3			
Rb								94.1	32.0
Cs								8.7	2.0
Ba								355	370
La	135	104	31	103	68			8.3	12.8
Ce	275	237	52	121	112			24.3	32
Sm	15.3	11.8	5.5					2.6	2.7
Eu	5.2	4.3		2.9	2.8			1.2	0.9
Tb	0.5	0.12	0.3	0.9	0.9				

ETF2, fumarole incrustations from NE crater, Etna, gypsum + sulfur, t=150°C. ETF4, similar to ETF2, contains more gypsum. ETF6, stalactites of Al sulfate in 420°C fumarole, SE crater, Etna. Trach and Etn are trachyte and etnaite from Etna; data after Condomines et al. [1982]. CV3 and CV6, stalactites of Al sulfate in fumaroles of 400°C, Colima. SH30, fumarole incrustations at Mount St. Helens, T>500°C, 1980 sample. SHA, Mount St. Helens ash of 1980, data after Sarna-Wojcicki et al., [1980] and Fruchter et al., [1980].

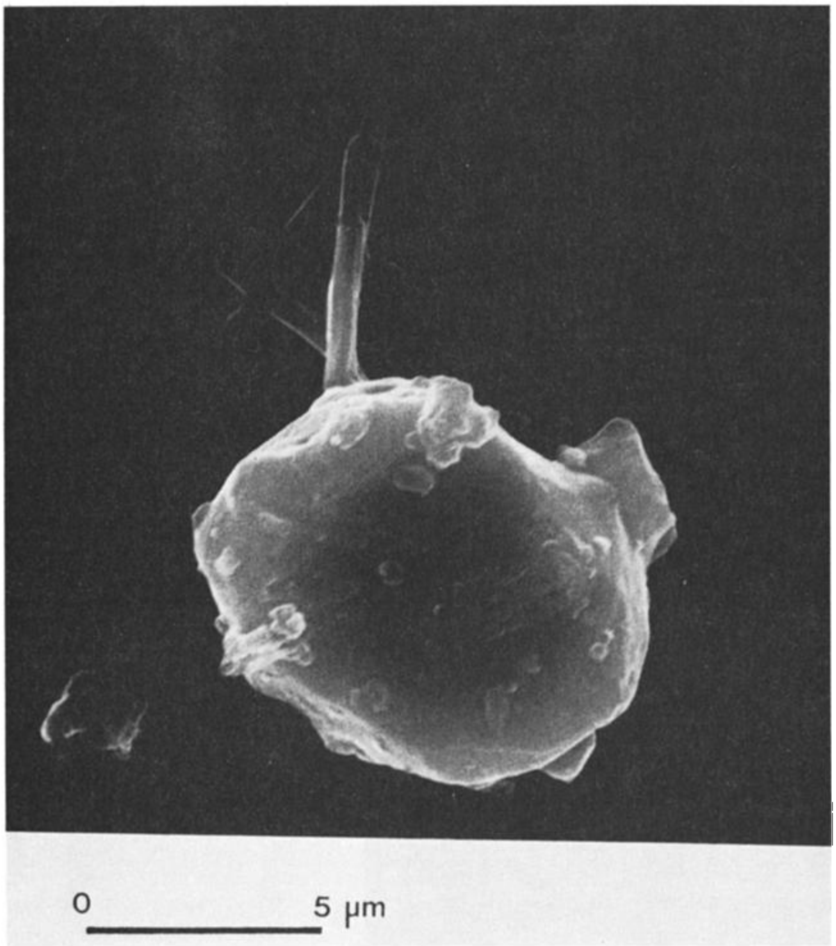

Fig. 9. $CaSO_4$ crystals overgrowing a silicate particle, 420°C fumarole, Etna.

presumed parent rock (Table 6). The REE were either transported in the vapor phase or derived from the parent rock by selective leaching, or both. Vapor transport of REE might occur as volatile fluor complexes. Ce-rich particles in volcanic plume samples were detected by W. I. Rose (personal communication, 1984) and M. Germani (Mount Erebus plume, Antarctica, unpublished results, 1985). No enrichments in REE were found in the Al sulfates of Etna and Colima, and in the Mount St. Helens samples. Apparently gypsum serves as a suitable host phase for the REE, not unlike some other Ca minerals (e.g., apatite), whereas Al sulfate is not a suitable host phase for REE.

The differences in plume particle chemistry between Etna and Mount St. Helens are striking: the Bocca Nuova plume is rich in Al and Fe sulfates and poor in (Na, K) chlorides, whereas the 1980 Mount St. Helens plume virtually lacks Al sulfates but is rich in chlorides. The high-temperature incrustations at Mount St. Helens are distinct because of their high Zn contents, whereas the gypsum incrustations at Etna are rich in REE.

The fundamental difference in plume particle load and element signature of the high-temperature fumarole incrustations is related to differences in magmatic gas composition, especially the F/Cl ratio [Oskarsson, 1981]. The F/Cl ratios from Etna and Colima are on average higher than at Mount St. Helens (Table 5). We suggest that at high F/Cl ratios, vapor transport

TABLE 5. F/Cl Ratios in Fumarolic Vapors

	F/Cl
Etna	
420°C	0.18
420°C	0.30
700°C	0.12
Average	0.20
Colima	
420°C	0.12
380°C	0.23
Average	0.18
Mount St. Helens	
Fumarole	0.11
Leachate	0.04
Average	0.08

Data from the 1980 fumaroles of Mount St. Helens after Casadevall and Greenland [1981] and Mount St. Helens ash leachate data after Evans et al. [1981]

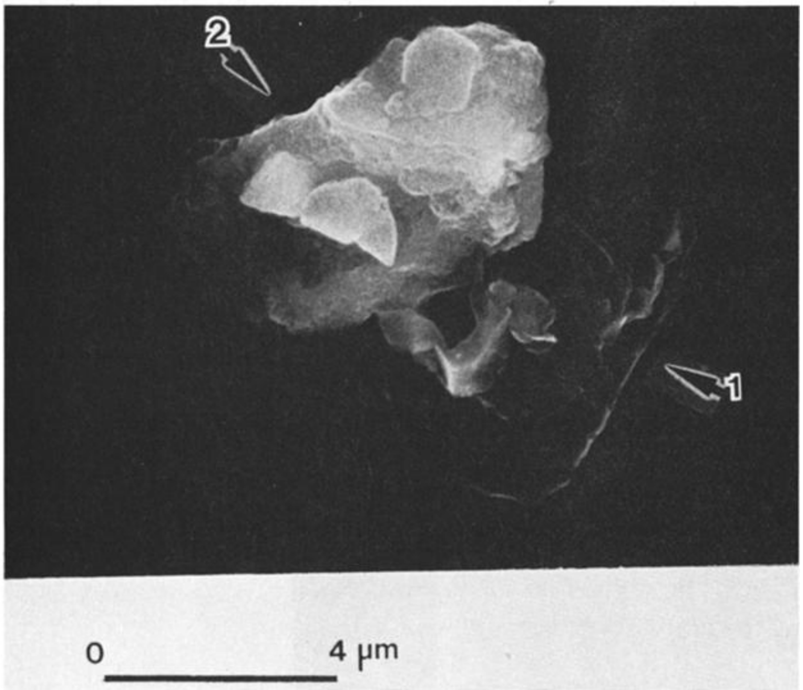

Fig. 10. $Al_2(SO_4)_3$ (dark grey, arrow 1), overgrowing silicate particle (bright, arrow 2), 700°C fumarole, Etna.

of Al and REE and possibly of other elements (e.g., Si) is common, whereas at low F/Cl ratios, Na, K, and metals are abundant in the vapor phase as chlorides. Thus the Mount St. Helens plume has a particle mineralogy and composition typical for a Cl-rich plume (with transport of Na, K, Rb, Cs, Zn, Cd, and Fe), whereas Etna displays the characteristics of a relatively F-rich plume, with vapor transport of Al and REE. The lack of chloride particles at Etna could be the result of alkali chloride deposition at vents on a partially frozen lava lake inside Etna's conduit [Le Guern, 1985], but the common occurrence of violent explosions in the crater during the sampling period and the presence of high-temperature sublimate phases (e.g., iron oxides) in the aerosol make this an unlikely explanation. Conversion of chlorides to sulfates in the plume might be an additional cause for the scarceness of chloride particles at Etna, although Na sulfate particles were rarely observed. The lack of chloride particles in the

TABLE 6. Element Enrichment Factors With Respect to Magma Normalized to Scandium

	ETF2 Trachyte	ETF2 Etnaite	ETF4 Trachyte	ETF4 Etnaite	ETF6 Trachyte	ETF6 Etnaite	SHA-SH30
Na							0.84
Fe							1.35
As							109
Cr			0.2	0.1	0.3	0.1	
Co	0.1	0.1	0.2	0.3	0.9	1.1	
Zn							156
Hf	0.3	0.6	0.3	0.6	1.1	2.4	0.7
Th	0.8	1.3	0.5	1.1	0.2	0.4	0.8
U							0.8
Rb							2.6
Cs							3.8
Ba							0.8
La	1.9	5.7	1.2	3.5	0.4	1.3	0.6
Ce	3.3	7.1	2.3	4.9	0.6	1.3	0.7
Eu	2.6	5.4	1.7	3.6			1.2
Tb	0.8	1.6	0.2	0.3	0.5	1	

See Table 4 for explanation of heads.

Fig. 11. Mixture of Al and Fe sulfate, overgrowing a silicate particle, 700°C fumarole, Etna.

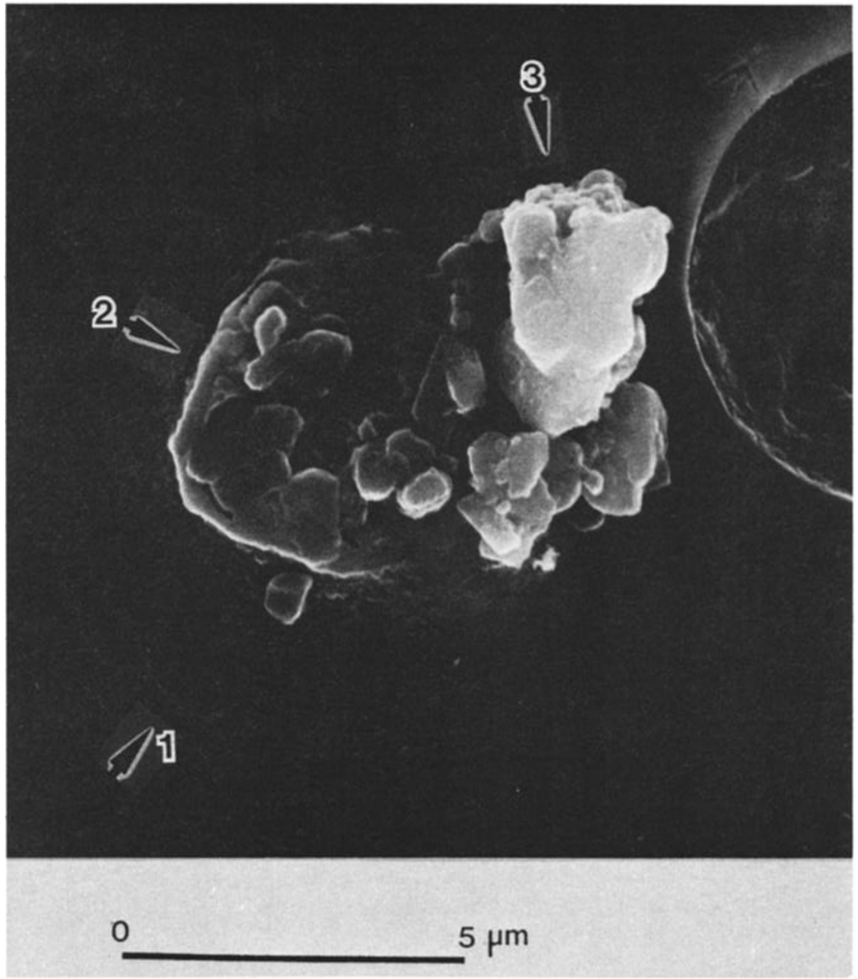

Fig. 12. F-rich aureole (arrow 1) around an Al sulfate particle (grey, arrow 2) and silicate grains (bright, arrow 3) on 8-μm filter, Bocca Nuova plume, Etna.

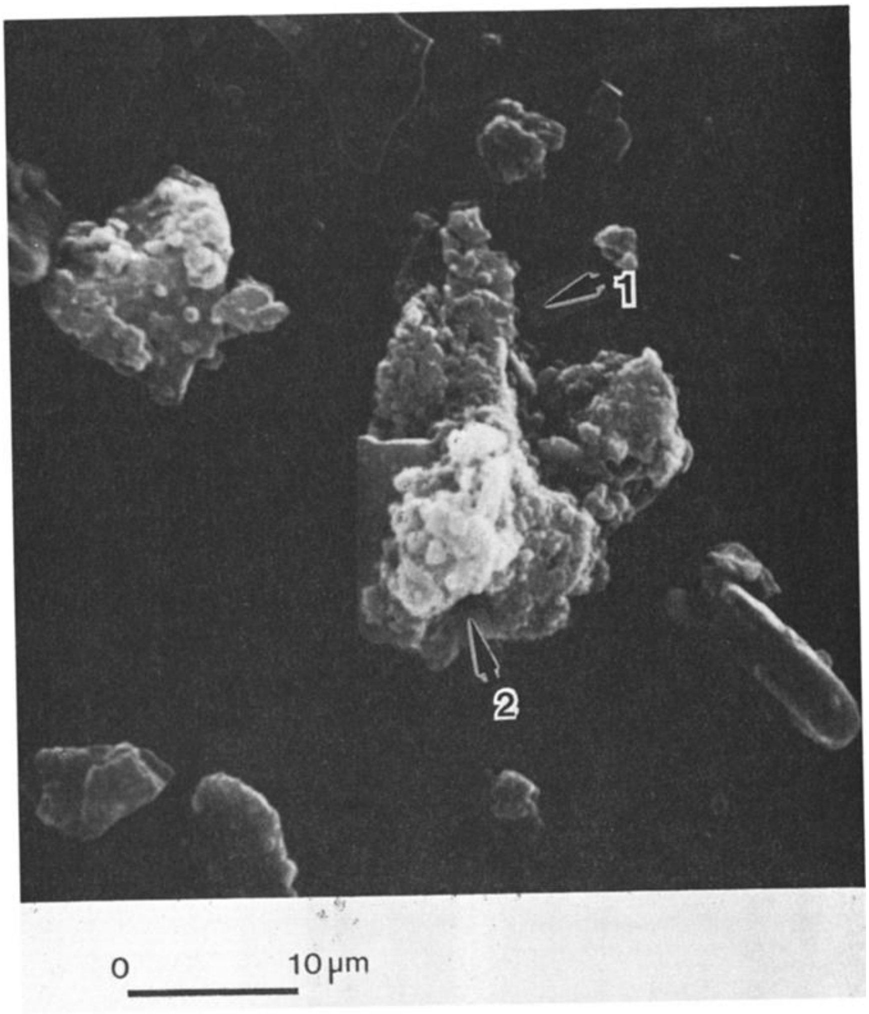

Fig. 13. Silicate particle from fumarolic incrustation, Mt. St. Helens crater, 1980. Overgrowths are $CaSO_4$ (irregular, grey, framboidal mass, arrow 1) and a crust rich in Pb and S (bright irregular mass, arrow 2).

Colima plume [Casadevall et al., 1984] and relatively high F/Cl ratios in the fumaroles point to an F-rich character for the Colima plume, and the abundance of Al sulfates in the Colima fumaroles strongly suggests vapor transport of Al.

Conclusions

Our data set indicates that different volcanoes have different plume particle chemistries and different element signatures of the high-temperature fumarole incrustations, probably related to different F/Cl ratios in the magmatic vapors. The data suggest vapor transport of Na and K as chlorides, and Al and possibly Ca as fluorides. We suggest that REE were mobile in the vapor phase at Etna and are transported as volatile F complexes. Vapor transport of Zn and Fe was common at Mount St. Helens, less intense for Zn at Etna and Colima, in agreement with the results of Smith et al. [1982].

Alkali-chloride particles appear to condense from the vapor phase relatively early (at high temperature, >500°C), whereas acid droplet formation is a late-stage process (below 330°C), resulting largely in sulfuric acid. Many earlier formed chloride particles react with the sulfate aerosol and are partially converted to sulfates. Plumes that have traveled tens of kilometers from the source will show complex textural relations and overgrowth patterns. The volume ratios of overgrowths and host particles suggest that many cations in condensation minerals were initially transported as vapors, although for specific cases leaching of ash particles can be invoked.

It has been suggested that hydrochloric acid emissions from volcanoes might be important in ozone conversions in the upper stratosphere [Johnston, 1980]. Our data indicate that chlorine in volcanic plumes is partly present as (Na, K) chloride particles, which may dissolve in water and can be removed from the plume relatively rapidly. During explosive eruptions a sizeable fraction of the emitted chlorine is returned to the surface of the earth with the ash (e.g., the 1982 El Chichon eruptions, [Varekamp et al., 1984; Mankin and Coffey, 1984]). Therefore most of the emitted volcanic chlorine will never reach the stratosphere and estimates of the chlorine flux from volcanoes to the atmosphere based on pre-eruptive volatile contents of the magma (e.g., from glass inclusion analyses) will lead to overestimates. Chlorine from the 1980 Mount St. Helens eruptions that reached the stratosphere occurred partly as particulates [Gandrud and Lazrus, 1981]. Reaction of such chloride particles with H_2SO_4 droplets to sulfates as described above for the Mount St. Helens plume will release HCl, which may react with stratospheric ozone [Woods et al., 1985].

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