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Water-Soluble Material on Aerosols Collected Within Volcanic Eruption Clouds

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In February and March of 1978, filter samplers mounted on an aircraft were used to collect the aerosol fraction of the eruption clouds from three active Guatemalan volcanoes (Fuego, Pacaya, and Santiaguito). The samples were collected on Teflon (Fluoropore) filters with a nominal pore diameter of 0.5 μm. The mass of air sampled by the filters ranged from 0.15 to 6.6 kg. The particulate material collected consisted of fragments of angular silicate ash and droplets of what is interpreted as dilute H_2SO_4 and HCl. After collection of the samples, each filter was rinsed with 60 ml of distilled-deionized water. Splits of each extract were centrifuged to remove particles greater than or equal to 0.1 μm in diameter, acidified, and analyzed for B, Ba, Be, Ca, Cd, Co, Cu, Fe, Li, Mg, Mn, Mo, Na, Pb, Si, Sr, V, and Zn by inductively coupled plasma–optical emission spectroscopy. Separate splits were analyzed for F and Cl by specific-ion-electrode methods and for U by a fission track technique. The elements dissolved in the aqueous extracts represent components of water-soluble material either formed directly in the eruption cloud or derived from interaction of ash particles and aerosol components of the plume. Calculations of enrichment factors, based upon concentration ratios, showed the elements most enriched in the extracts relative to bulk ash composition were Cd, Cu, V, F, Cl, Zn, and Pb. These elements represent a subset (with the addition of Cl and F) of elements previously reported enriched in atmospheric aerosols in remote regions as well as in volcanic areas. This suggests that some of the enriched elements were widely dispersed as volatile halides emitted from a volcanic source.

INTRODUCTION

Particulate matter is contributed to the atmosphere by both natural and anthropogenic sources. Man's major contribution of small particles to the atmosphere originates from his varied industrial and agricultural activities. Natural sources include the oceans, crustal weathering, and volcanic eruptions. Analysis of particulate matter in the atmosphere is important in evaluating the relative input from each source. Recent interest in small particles in the atmosphere has centered on the concern that man might inadvertently affect weather, visibility, human health, and biota in general by changing the distribution of particles in the atmosphere on a global scale. In order to evaluate this hypothesis, it is necessary to fully understand the type and amount of particulate material input to the atmosphere by the various natural sources.

Previous efforts were made to collect and analyze atmospheric particulate material from geographically remote locations such as the Antarctic Polar Plateau to study the composition of the background aerosol [*Zoller et al.*, 1974; *Duce et al.*, 1975; *Buat-Menard and Chesselet*, 1978; *Maenhuat and Zoller*, 1977; *Maenhuat et al.*, 1979]. Particles were collected by ground-based or ship-based samplers consisting of some type of filter and a high-volume pump. The filter samples were analyzed for trace metal content by a combination of flame and flameless atomic absorption spectrophotometry and instrumental neutron activation analysis (INAA). The source of a particular atmospheric trace element was evaluated by calculating the ratio of the concentration of that element to the concentration of a reference element. Reference elements were generally those considered relatively nonvolatile yet ubiquitous in atmospheric aerosols and present in high concentrations in the source of interest (e.g., Al or Si). The atmospheric ratio was then compared with the corresponding ratio in the source. The calculations indicated that Al, Sc, Th, Sm, Mn, Eu, Fe, La, Ce, Co, Cr, Na, K, Mg, and Ca were derived from either crustal weathering or the ocean. The elements In, W, Au, As, Ag, V, Zn, Cu, Hg, Cd, Sb, Pb, Se, and Br were found to be present in the particulate matter in concentrations too high to be explained by an origin from either crustal weathering or seawater.

Studies using similar sampling techniques were carried out near urban areas [*Gordon et al.*, 1974; *Rahn*, 1975; *Miklishanskiy et al.*, 1977, 1978]. The group of trace metals anomalously enriched in these samples was the same as that found in remote locations. The relatively high volatility of these elements and many of their compounds suggested that high-temperature volatilization from crustal material was responsible for dispersing the enriched elements [*Zoller et al.*, 1974; *Goldberg*, 1976]. The fact that the same elements were similarly enriched in widely separated locations, some very remote from industrial activity, suggested that sources

for these elements were natural and widely dispersed [*Duce et al.*, 1975].

Among the natural sources of the enriched elements, volcanism is potentially significant [*Mroz and Zoller*, 1975]. Analysis of filter samples from ground-based collectors showed an enrichment of Cu, Zn, Hg, Sb, Pb, Se, and Br in atmospheric aerosols from the active volcanic regions of Hawaii, Iceland, and Sicily [*Cadle et al.*, 1973; *Mroz and Zoller*, 1975; *Buat-Menard and Arnold*, 1978]. Samples of atmospheric particulate material collected in the plume of Augustine volcano, Alaska, showed enrichment of Zn, Cu, Au, Pb, As, Cd, Cl, Br, Se, Sb, Hg, and S [*Lepel et al.*, 1978]. In an attempt to detect historical volcanic eruptions by chemical analysis of an ice core from Greenland, *Herron and Langway* [1978] found that S, Zn, Cd, Cu, and Pb were anomalously enriched in certain layers of the ice. They concluded that volcanism was the source of these elements in atmospheric aerosols, which eventually fell as precipitation and became incorporated into the ice sheet.

The present study is part of a cooperative research project designed to characterize the physical and chemical properties of particulate matter injected into the atmosphere by explosive volcanic eruptions. The sampling procedures represent an improvement over earlier studies of this phenomenon because material was collected inside the eruption cloud and because the work emphasized study of small ($\leq$25-μm diameter) particles. A knowledge of the character of the small particles is important because their longer residence time in the atmosphere makes them very important in evaluating the effects of volcanic eruptions on atmospheric chemistry and climate [*Rose et al.*, 1980].

Specifically, the sampling took place in February and March 1978. The National Center for Atmospheric Research (NCAR) sponsored the project which sampled eruption clouds over the active volcanoes Fuego, Pacaya, and Santiaguito in Guatemala. A specially equipped Beech Queen Air aircraft was used to make 11 sampling flights during which various experiments were conducted [*Rose et al.*, 1977; *Cadle et al.*, 1979]. The flights were planned to allow for sampling directly within the most intense part of the eruption cloud as well as downwind from the volcanic vent where the cloud was more diffuse.

VOLCANIC ACTIVITY DURING SAMPLING FLIGHTS

Fuego

Starting in September 1977 and continuing throughout the sampling flights, Fuego was in constant low-level pyroclastic activity. This represented a departure from its 20-year pattern of short-lived, frequent, violent pyroclastic eruptions [*Rose*, 1978]. In February 1978, mild Vulcanian activity producing large amounts of ash was interspersed with vaporous, ash-poor clouds. Both types of eruptions were sampled.

Pacaya

Pacaya has been continuously active since 1965 [*Rose*, 1967; *Eggers*, 1971]. During this time, the volcano has alternated between mild Strombolian activity, with occasional lava flows, and explosive Vulcanian activity [*Rose*, 1978]. At the time of sampling, it was in a state of intense vapor emission with little or no ash being erupted.

Santiaguito

Santiaguito is a Pelean Dome which has been continuously erupting since 1922 [*Rose*, 1972, 1973]. Since April 1975 the

volcano has been producing several pyroclastic eruptions each day with some reaching heights of more than 5 km [*Rose*, 1978]. During the sampling flights, this activity continued to produce large, ash-rich eruption clouds.

EXPERIMENTAL PROCEDURE

The samples for this study were collected on filters mounted on the aircraft. Air was introduced to the filters through an aluminum tube with its intake at the nose of the plane. Each sampler consisted of three separated filters mounted in series in a stainless steel holder. The first filter in the series was a Teflon filter (Fluoropore) with a nominal pore diameter of 0.5 μm and a filtration efficiency of greater than 99.99% over the particle size range 0.03–1.0 μm [*Liu and Lee*, 1976]. This filter was used to collect particles without appreciable absorption of gases. The following two filters were cellulose (Whatman) filters impregnated with tetrabutylammonium hydroxide to retain acid gases. Following the sampling flights, each filter was rinsed with 60 ml of distilled-deionized water. This rinse was designed to remove a representative fraction of the water-soluble material present on the surface of the filter. No attempt was made to remove all water-soluble material or to attack material trapped in the webbing of the filter where water might not reach because of the hydrophobic nature of the filter material. Splits of these extracts containing water-soluble material and fine ash particles were given to several coinvestigators for further analysis.

In this study, particles greater than or equal to 0.1 μm in diameter were removed from each aqueous extract of the Fluoropore (particulate) filter by centrifugation. A few milliliters of the clear, centrifuged extract were acidified to pH less than 2 with sub-boiling-distilled HNO$_3$ and analyzed for B, Be, Ba, Ca, Cd, Co, Cu, Fe, Li, Mg, Mn, Mo, Na, Pb, Si, Sr, V, and Zn by inductively coupled plasma–optical emission spectroscopy. Additional aliquots were analyzed for F and Cl by specific-ion-electrode methods, Uranium in solution was determined by a fission track method [*Fleischer and Lovett*, 1968; *Reimer*, 1976]. The extracts of the cellulose (Whatman) filters were not analyzed in this study because initial measurements of unused filters showed variable and excessive blank levels for most of the trace metals of interest.

Two types of blank corrections were made for each analyzed extract of the Fluoropore filters (Table 1). The first, a 'filter-handling' blank, consisted of the aqueous extract of a Fluoropore filter that had undergone all the manipulations of the sample filters except for having air passed through it. The concentration of an element in the blank was subtracted from the concentration of the same element in the extract. The second blank, here termed the 'atmospheric' blank, consisted of the aqueous extract of a Fluoropore filter that sampled 6.6 kg of air in northern Guatemala away from direct volcanic influence. The concentration of an element in the extract of this filter was first corrected for the 'filter-handling' blank. For the elements remaining above blank, the total number of micrograms in the 60 ml of 'atmospheric' extract was calculated and this amount was divided by the 6.6 kg of air sampled. These values were subtracted from the sample value similarly normalized to 1 kg of air. It is assumed that the two blanks measured are representative of the major sources of contamination and that the elemental concentration values re-

TABLE 1. Blank Data on Extracts of Fluoropore Filters

Element	'Filter-Handling' Blank, μg/l of Extract	'Atmospheric' Blank, μg/kg of Air
B	<3	<0.027
Ba	<1	<0.0091
Be	<0.5	<0.0046
Ca	110	3.6
Cd	2.8	0.021
Cl	160	1.4
Co	<2	<0.018
Cu	5.0	0.022
F	3.0	0.12
Fe	14	1.5
Li	<2	<0.018
Mg	48	1.6
Mn	1.1	0.061
Mo	<10	<0.091
Na	<100	1.5
Pb	5.5	0.029
SiO_2	80	6.0
Sr	<0.3	0.013
U	0.48	0.0022
V	9.5	0.086
Zn	17	0.082

ported above blank are actual contributions from the volcanic events.

The procedure used in this study was designed to identify and characterize the chemical lability of the most mobile elements associated with freshly erupted, very fine grained particulate material. These elements are the first to be released on exposure of the particles to torrential rains, which frequently accompany explosive eruptions. If one assumes that the group of elements found by previous workers to be anomalously enriched in atmospheric aerosols originated by volatilization during a volcanic eruption, then the same elements should be enriched in this mobile component of the particles.

RESULTS AND DISCUSSION

The results of the aqueous extraction of the Fluoropore filters are presented as micrograms of element extracted per kilogram of air sampled (Table 2). The elemental concentrations in the extracts generally vary by an order of magnitude or more. This large variation is similar to that observed in water leachates of ground-collected air-fall ash from the same volcanoes [Smith, 1980].

In order to determine which elements show relative en-

richments in a water-soluble form as compared to abundances in bulk ash material and to avoid difficulties in relating the absolute concentration of a given element in a filter extract to its concentration in ash, an enrichment factor (EF), based upon concentration ratios, was calculated by the following formula:

$$EF = \frac{(X/Mg)_{extract}}{(X/Mg)_{ash}}$$

where X is the concentration of the element of interest. Magnesium was chosen as the reference element because of its easily measured concentration in the ash, the relatively refractory nature of its compounds, and because it occurs in reliably measured, above-blank concentration in a maximum number of extracts. An EF close to unity indicates there is essentially no enrichment occurring for a given element in a water-soluble form relative to the abundance expected from congruent dissolution of ash (i.e., $(X/Mg)_{extract} = (X/Mg)_{ash}$). A value less than one indicates preferential solution of magnesium relative to the element of interest, and a value greater than one indicates preferential solution of an element relative to that expected from congruent dissolution of ash.

TABLE 2. Atmospheric Concentration (Micrograms Element/Kilogram Air) of Water-Soluble Elements

Date in 1978	Volcano	Distance From Vent, km	Air Mass, kg	Ca	Cd	Co	Cu	Fe	Mg	Mn	Na	Pb	Si	Sr	V	Zn	F	Cl
Feb. 8	Pacaya		5.8	...*	0.089	...	...	...	...	...	0.10	...	...	...	...	0.18	...	...
Feb. 8	Pacaya		1.6	...	...	...	...	...	...	...	...	0.065	...	...	...	0.60	...	...
Feb. 8	Pacaya		0.27	12.	...	...	...	6.5	6.8	0.069	20.	...	...	0.051	...	0.14	...	21.
Feb. 10	Fuego		2.0	...	...	...	...	...	...	...	...	0.33	...	...	...	...	...	...
Feb. 10	Fuego		1.8	...	...	...	...	...	...	...	...	...	...	...	0.065	...	...	...
Feb. 19	Fuego	15–20	1.15	260.	...	0.78	0.35	180.	150.	3.8	46.	0.054	510.	1.9	0.094	0.44	12.	2.3
Feb. 19	Fuego	0.33–0.57	0.19	31.	...	...	1.9	34.	14.	0.26	...	0.22	98.	0.29	2.3	...	15.	46.
Feb. 22	Santiaguito	3–8	0.15	12.	0.66	...	...	16.	2.4	0.059	...	...	35.	...	0.11	...	2.7	55.
Feb. 22	Santiaguito	3–18	4.5	...	...	...	...	...	...	...	...	...	...	...	0.044	...	0.13	0.20
Feb. 27	Fuego	3–13	2.2	23.	...	0.10	0.022	22.	18.	0.43	2.9	...	51.	0.19	0.18	...	6.2	2.1
Feb. 27	Fuego	25–33	1.46	91.	0.099	0.35	0.16	94.	90.	1.7	14.	...	210.	0.73	0.30	0.33	3.7	1.9
Feb. 27	Fuego	5–8	1.25	270.	0.046	0.58	6.4	160.	130.	3.1	52.	3.8	510.	2.0	0.084	0.69	34.	6.8
Feb. 28	Santiaguito	32–35	2.1	93.	0.079	0.071	0.18	15.	7.8	0.51	21.	...	89.	0.59	0.10	0.43	11.	8.6
Feb. 28	Santiaguito	10–12	1.23	24.	0.22	...	0.046	4.8	0.90	0.22	5.8	...	18.	0.16	0.37	1.0	3.6	8.6

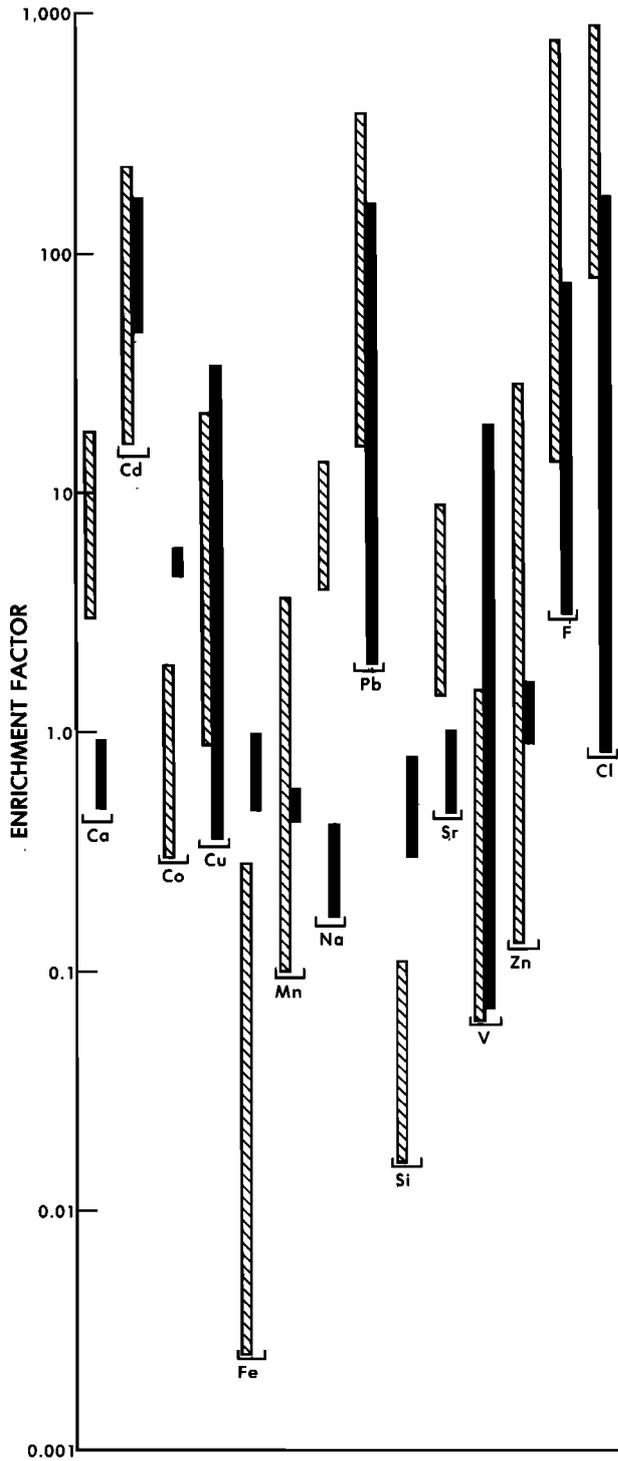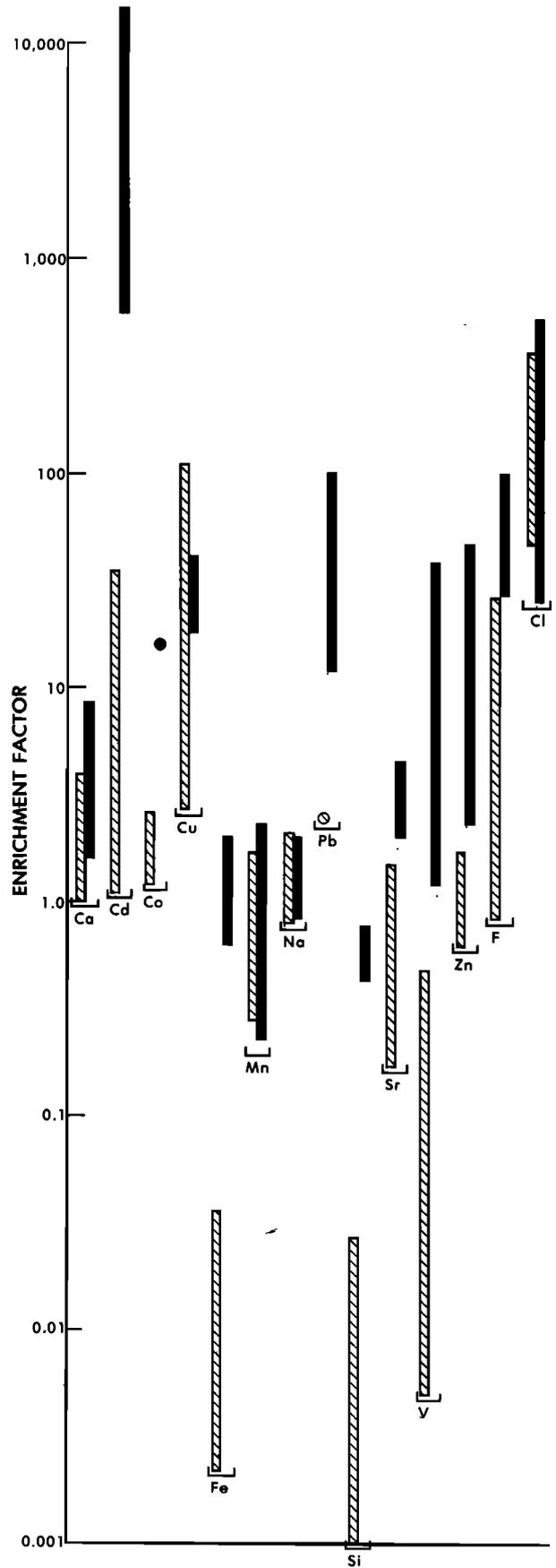*Dots indicate below blank level (see text for blank corrections used).

Fig. 1a

Fig. 1. Comparison of enrichment factors of water extracts of particles collected on Fluoropore filters during airborne sampling of eruption clouds (solid) and water leachates of air-fall ash from the same volcano (striped). (a) Fuego volcano. (b) Santiaguito volcano. (c) Pacaya volcano.
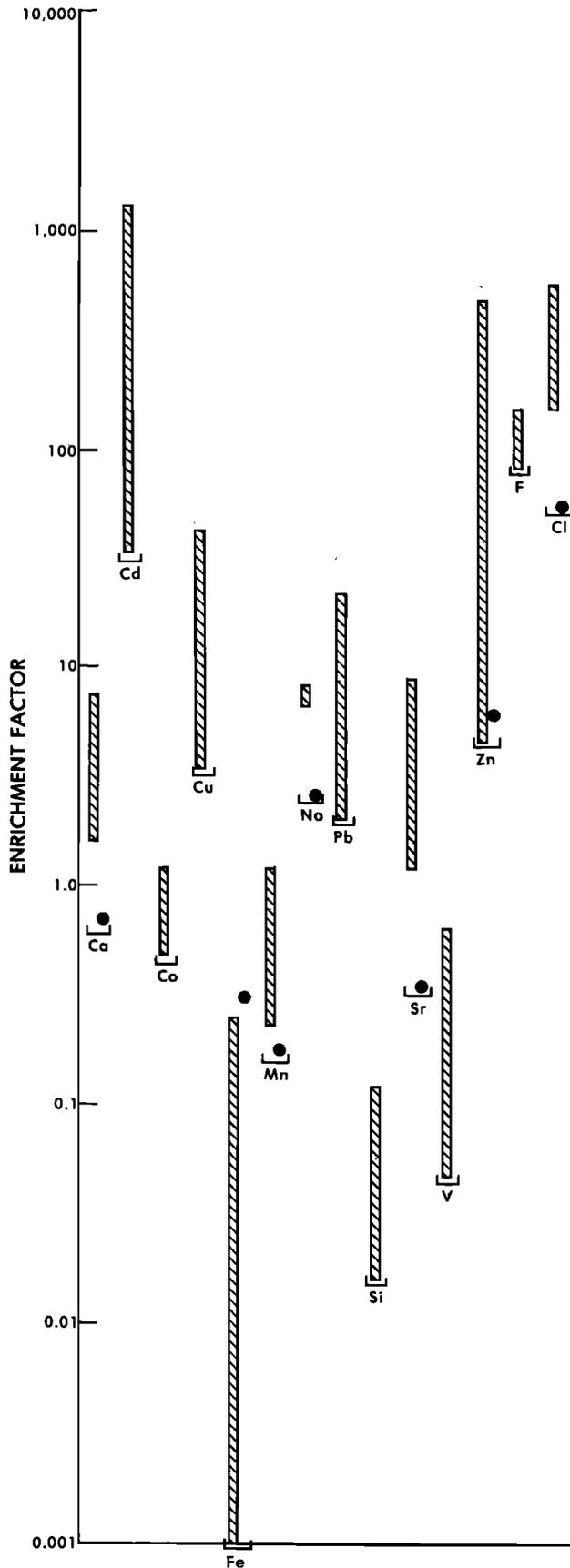
Fig. 1b

Fig. 1c

Denominators for the various enrichment factors are based upon calculated average compositions of air-fall material collected previously from the same volcanoes [*Rose et al.*, 1977, 1978a; W. I. Rose, Jr., unpublished data 1978]. Because the composition of ash erupted from a given volcano can vary with time [*Rose et al.*, 1978a], an additional source of error is introduced by this procedure. However, variations of the denominator ratio caused by magmatic compositional evolution are not likely to be large enough to cause the order of magnitude variation observed in many of the enrichment factors. In order to minimize the effect of denominator variations, an element was considered significantly enriched or depleted, relative to Mg and the ash, only if the EF value was greater than 10 or less than 0.1, respectively.

High Si values in the extracts (Table 2) indicate that centrifugation may not have removed all the fine ash particles (primarily aluminosilicate material). Any contaminating particles in the extract will lower high EF values and raise low EF values so that an EF of 1 is approached. Thus in an extract with possible contamination by ash particles, an element showing significantly high enrichment is even more enriched than the calculated EF indicates. With this in mind, the pattern of EF values for the extracts shows some interesting trends.

Figure 1 shows the range of EF values for all the elements found in above-blank concentrations. For comparative purposes, Figure 1 also shows the range of EF values calculated using analyses of water leachates of the freshly erupted air-fall ash samples discussed by *Smith* [1980]. The possibility of contamination of these water leachates by ash particles is considerably reduced because each sample was filtered through a Millipore filter with a nominal pore size of 0.1 μm. The Pacaya data are represented in the figure as points rather than ranges because only one aqueous extract from this volcano contained magnesium in above-blank concentration. Unlike the ash-rich plumes of Fuego and Santiaguito, Pacaya was in a state of vapor emission during sampling. The lower concentrations of some leachable elements in the Pacaya plume (Table 2) may relate to this difference in eruptive style. Apparent association of leachable elements with high ash content implies that much soluble material is associated with ash surfaces.

A characteristic suite of elements is significantly enriched in the aqueous extracts. Fuego and Santiaguito both contain anomalously high concentrations of Cd, Cu, V, F, and Cl in water extracts of their ash. Other elements with anomalous enrichment factors include Pb (Fuego) and Zn (Santiaguito). A similar group of elements are enriched in water leachates of ground-collected ashes. Fuego and Santiaguito air-fall ashes both contain enrichments of Cd, Cu, F, and Cl. In addition, Fuego ashes are also enriched in Ca, Na, Pb, and Zn. The elements enriched in the water extracts of airborne Fuego and Santiaguito ashes are subsets (with the addition of Cl and F) of the elements reported enriched in atmospheric aerosols by previous workers as cited in an earlier section. Although not determined in this study, it is probable that the aqueous extracts are also highly enriched in sulfate. *Stoiber and Bratton* [1978] found that the three volcanoes studied each emitted from 300 to 1500 metric tons of SO$_2$ per day. *Taylor and Stoiber* [1973] and *Rose et al.* [1978a] showed that sulfate was a major component of water leachates of freshly erupted ashes from Guatemalan volcanoes.
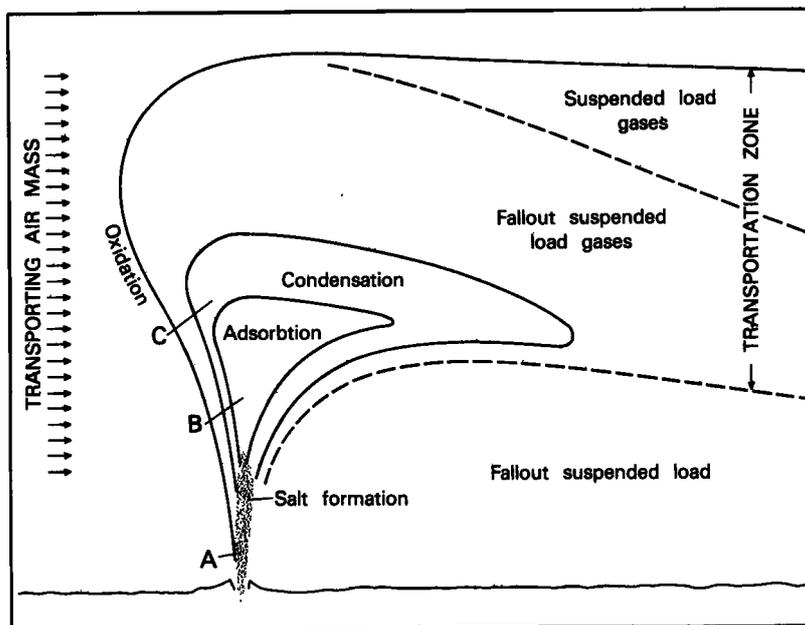
Fig. 2.   Hypothetical shape of a plinian eruption column. The zones A, B, and C refer to temperature-dependent processes discussed in the text. (Adapted from *Óskarsson* [1978].)

It should be noted that the elements B, Ba, Be, Li, Mo, and U were not detected in the extracts at above-blank concentrations. Calculations show, however, that the blank values of some of these elements (Table 1) can result in an

EF value greater than 1. Thus the possibility that some or all of these six elements are enriched in the extracts must not be ruled out.

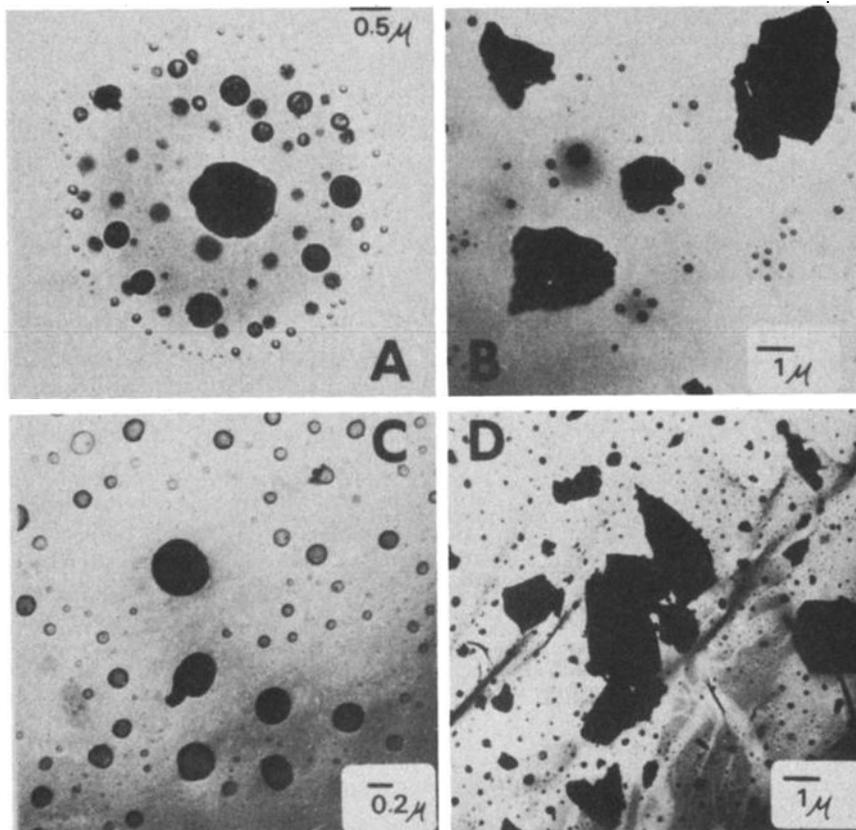Water-soluble material collected by the Fluoropore filters

Fig. 3.   Transmission electron micrographs of particles collected from Fuego eruption cloud of February 11, 1978 [from *Rose et al.*, 1980]. (*a*) Probable H_2SO_4 particle. (*b*) Larger angular silicate particles and acid droplets. (*c*) Field of droplets. (*d*) Angular silicate particles and smaller droplets.
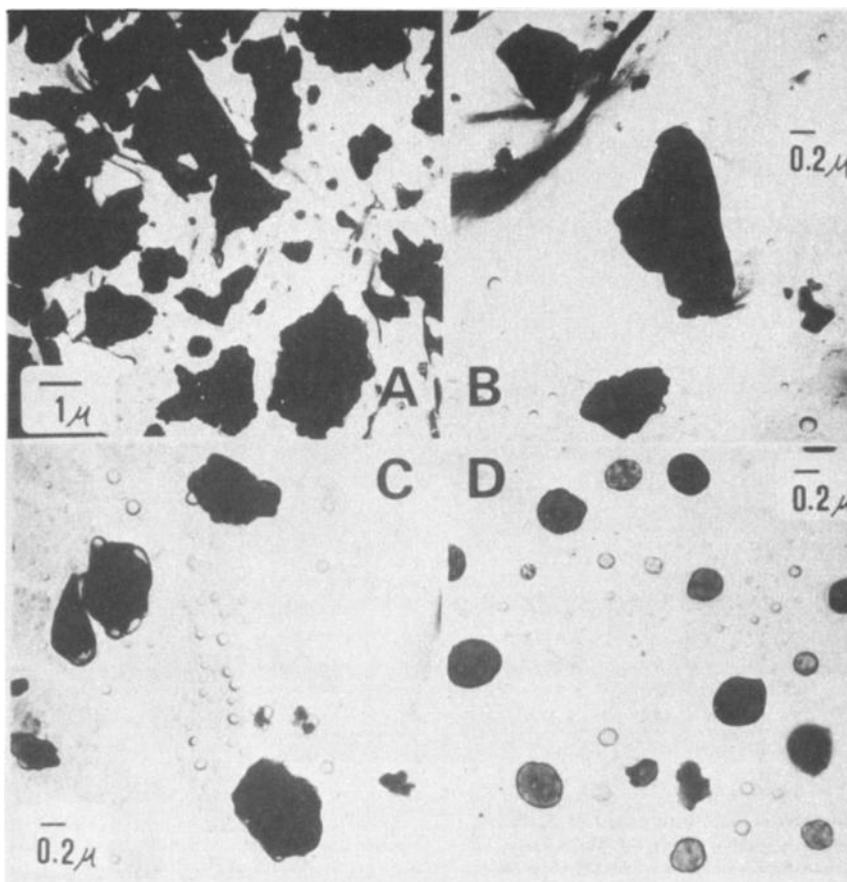
Fig. 4. Transmission electron micrographs of Santiaguito eruption cloud particles [from *Rose et al.*, 1980]. (*a*) Angular silicate particles and smaller droplets. (*b*, *c*) Particles with droplets adhering and small discrete droplets. (*d*) Field of droplets.

is produced during interactions of ash particles with gaseous and aerosol components of the eruption cloud. *Óskarsson* [1978, 1980] proposed three temperature-dependent processes within an eruption cloud which affect the type and amount of soluble material on ash particles (Figure 2). At high temperatures in the eruption vent and the core of the eruption cloud, microscopic salt particles crystallize (primarily chlorides, fluorides, and sulfates of the alkali metals and calcium). This process is shown as zone A in Figure 2. An upper limit for the temperature of salt crystallization is set by the melting point of the salt being formed. For example, the melting point of NaCl is 801°C and of $CaSO_4$ is 1450°C. At temperatures below 340°C, H_2SO_4 is stable and may condense as an aerosol (zone C). At temperatures between those for salt crystallization and H_2SO_4 formation, *Óskarsson* [1978, 1980] has suggested that adsorption of HCl and HF gas onto the surface of solidified silicate material may be important (zone B).

The relative importance of these three processes is unknown, but there is some positive evidence for condensates of salts and H_2SO_4 aerosols in the eruption clouds of the Guatemalan volcanoes studied. Studies of ash particles by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) coupled with energy dispersive X ray analysis (EDXRA) show salt crystals independent of ash

as well as acid droplets coating ash particles [*Rose et al.*, 1980]. Figures 3 and 4 show transmission electron micrographs of unsized filter samples of particles collected in the Fuego and Santiaguito eruption clouds, respectively. The particles consist of small droplets and larger angular fragments. Figure 3a shows a pattern of droplets typical of H_2SO_4 morphology [*Rose et al.*, 1980]. In Figure 4c some of the angular fragments have a coating of droplets. Energy dispersive X ray analysis with the SEM showed most of the angular fragments were silicates. Some tabular nonsilicate crystals high in Ca and S were inferred to be $CaSO_4$.

Figures 5 and 6 show SEM images of particles collected in the Santiaguito eruption cloud. Figure 5b shows a tabular particle with EDXRA pattern of $CaSO_4$ [*Rose et al.*, 1980]. Such salt particles which are independent of ash are evidence for a salt formation zone in the plume [*Óskarsson*, 1978, 1980]. The particles in Figure 6 were collected on stage 3 of the 10-stage piezoelectric cascade impactor designed to sample different particle size fractions. The diameter of particles collected with 50% efficiency was 6.4 μm for this stage. The droplets in Figure 6c gave S peaks on EDXRA and were interpreted to be dilute sulfuric acid. The rings around the angular fragments in Figure 6d are thought to be residual acid coatings.

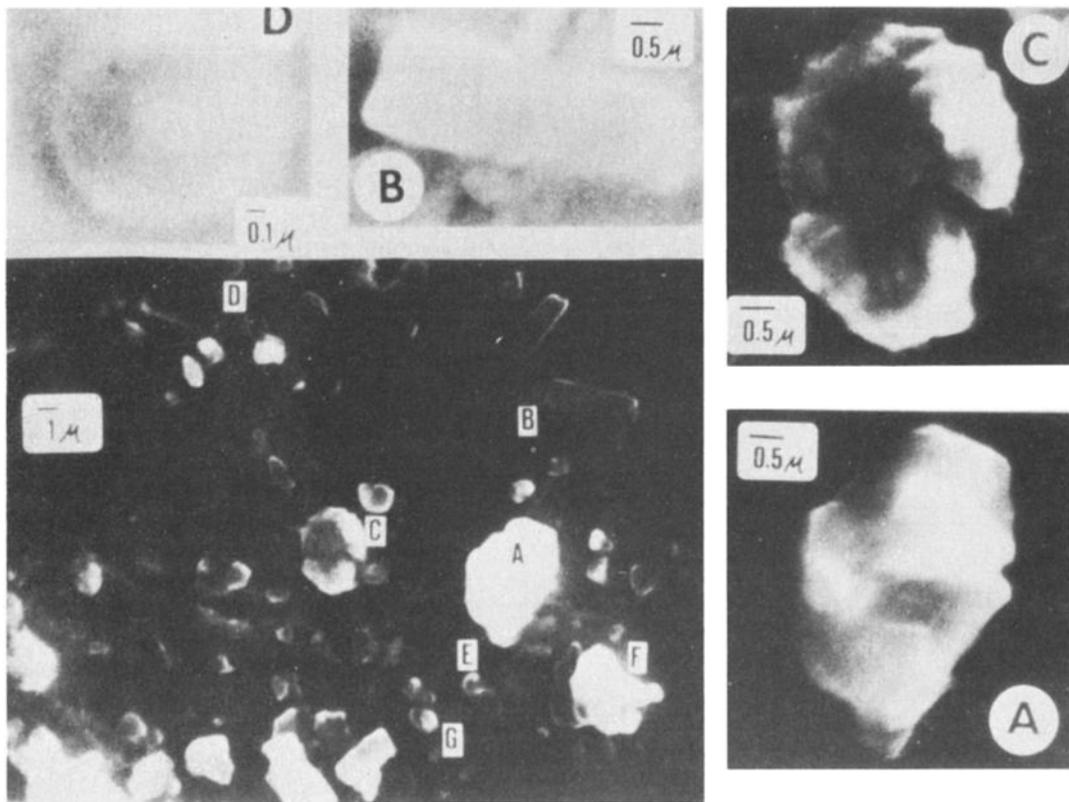The acid which coats some of the small particles may

Fig. 5. Scanning electron microscope imagery of Santiaguito eruption cloud particles of February 22, 1978 [from *Rose et al.*, 1980]. Lower left shows field of particles. (*a*, *f*) Angular particles with EDXRA pattern of $CaSO_4$. (*c*) Angular particle with EDXRA pattern of plagioclase. (*d*, *e*, *g*) Spherical particles with sulfur peak in EDXRA pattern (probable H_2SO_4).
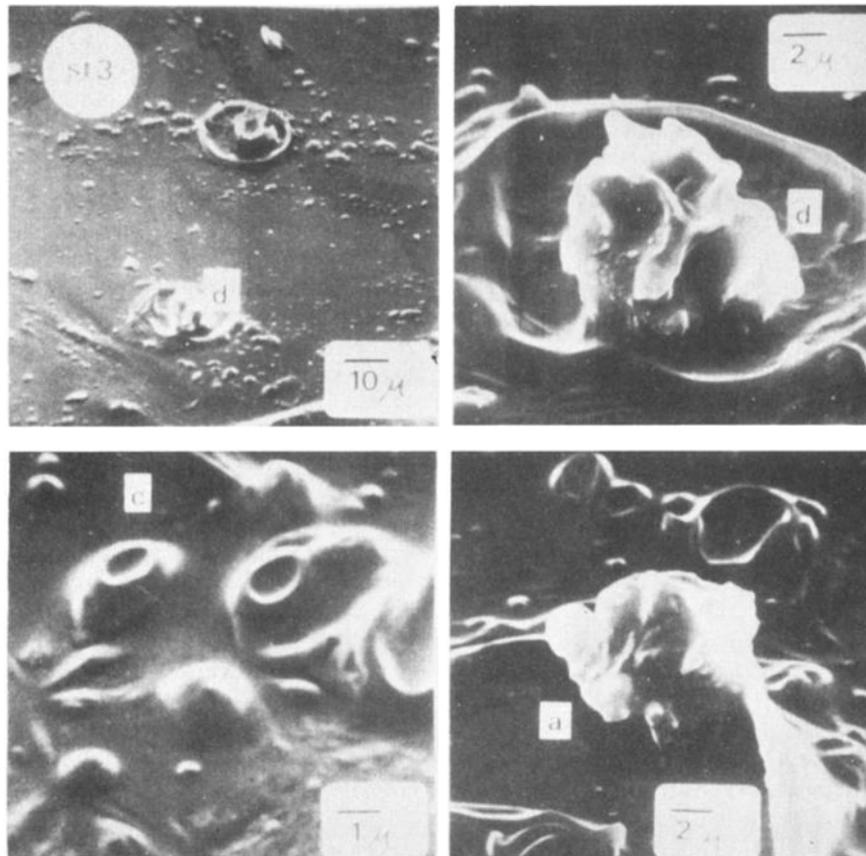

Fig. 6. Scanning electron microscope imagery of particles collected on stage 3 of cascade impactor from Santiaguito eruption cloud of February 28, 1978 [from *Rose et al.*, 1980]. (*a*) Angular particle which EDXRA shows is similar to rhyolite glass. (*c*) Droplets with indentations (partially evaporated) which give sulfur peaks on EDXRA. (*d*) Shard-shaped angular fragment with EDXRA pattern of rhyolite glass.

congruently (within a factor of 10) leach some elements from the silicate constituents of the ash (primarily glass and feldspar). On evaporation of this acid, the residue on particle surfaces would be available for rapid mobilization on contact by water. This process may partially account for the measured elements that were not anomalously enriched in the water extract.

The processes responsible for the production of soluble material on ash seem to be quite similar to those which operate during the formation of fumarole incrustations. The incrustation mineral assemblages, dominantly sulfates and halides, are thought to form by (1) condensation of volatile halides [Óskarsson, 1979] and/or (2) reaction of acidic volcanic gas with the atmosphere and the fumarole wallrock [Stoiber and Rose, 1974]. These two processes are analogous to those occurring in the condensation and adsorption zones [Óskarsson, 1978, 1980] of a volcanic eruption cloud.

CONCLUSIONS

A study of water-soluble material on fine ash particles collected in volcanic eruption clouds has led to the following conclusions:

1. Certain elements are anomalously enriched in a water-soluble form on the ash relative to bulk ash composition. These elements include Cd, Cu, Pb, Zn, V, F, Cl, and probably S (as sulfate). The anomalously enriched cations were probably emitted from the volcano as volatile halides or sulfates and either condensed directly onto ash particles or dissolved in acidic aerosols which then condensed onto the ash.

2. The measured elements that were not anomalously enriched in the extract relative to the bulk composition of ash probably represent congruent (within a factor of 10) leaching of fine silicate ash particles (primarily feldspars and glass) by the acid droplets which frequently coat them.

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