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Atmospheric Implications of Studies of Central American Volcanic Eruption Clouds

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During February 1978 a group of scientists from the National Center for Atmospheric Research, several colleges and universities, the U.S. Geological Survey, and NASA used a specially equipped Beech Queen Air aircraft to make 11 sampling flights in Guatemala through the eruption clouds from the volcanoes Pacaya, Fuego, and Santiguito. Measurements were made of SO_4^{2-} , SO_2 , HCl, HF, and 11 cations that were in water-soluble form, on samples collected by a specially designed filter pack. Particle size distributions were obtained with a piezoelectric cascade impactor, and the particles were identified by energy dispersive X ray analysis. Evacuated canisters were flown to obtain samples for gas chromatographic analysis. Some of the conclusions reached are that since most of the sulfur was found to be in the form of SO_2 , the H_2SO_4 droplets resulting from major explosive eruptions must largely result from the reaction of SO_2 with OH, at the same time depleting the atmosphere of OH; the volume concentration ratio $[\text{SO}_2]/[\text{HCl}]$ always somewhat exceeded unity; and the amount of fine ash remaining in the stratosphere for long periods of time may depend on the crystallinity of the magma. Correlation spectrometry showed that each volcano was emitting 300–1500 metric tons of SO_2 per day.

INTRODUCTION

Volcanic emissions to the atmosphere have been primarily responsible for the formation of our atmosphere and oceans. Furthermore, large explosive eruptions often inject material into the stratosphere that remains there for a year or more and affects the chemistry of the stratosphere and the earth's radiation balance. The huge amounts of sulfur dioxide that are generally assumed to be erupted into the stratosphere by an eruption such as that of Gunung Agung in Bali in 1963 may markedly deplete the stratosphere of OH by the reaction



for many months, and the sulfuric acid droplets formed from the HSO_3 scatter and absorb radiation [Cadle and Grams, 1975]. The sulfuric acid droplets and volcanic ash may take part in heterogeneous reactions [Cadle *et al.*, 1975], and volcanic hydrogen chloride may affect the ozone content of the stratosphere to an appreciable extent [Cadle *et al.*, 1976]. During the last 2 decades, eruptions by several volcanoes have produced eruption clouds that have penetrated into the stratosphere. Eruptions by Agung in 1963 and by Vulcán Fuego in Guatemala in 1974 were especially violent. Observations of normal-incidence solar radiation of Mauna Loa Observatory in Hawaii have shown that in 1977, for the first time since the Agung eruption in 1963, the values have returned to those measured in 1958–1962 [Mendonca *et al.*, 1978].

The particulate material in explosive eruption clouds consists largely of volcanic ash (that is, finely divided lava) and droplets of impure sulfuric acid. However, most of our knowledge of the nature of this material has been based on studies of ash deposits on the ground, although limited studies of col-

lected ash have been made from aircraft [e.g., Cadle *et al.*, 1969; Hobbs *et al.*, 1977]. The determinations of the gaseous emissions from explosive volcanoes have been limited to emissions from fumaroles and from craters between explosive eruptions.

To obtain more direct information concerning the composition of eruption clouds from explosive volcanoes a group of scientists from the National Center for Atmospheric Research, several colleges and universities, the U.S. Geological Survey, and NASA used a specially equipped Beech Queen Air aircraft to make 11 sampling flights in Guatemala through the eruption clouds from the volcanoes Pacaya, Fuego, and Santiguito, during February 1978. During our sampling, Pacaya was in a state of intense vapor emission, and when vapor emission abated, glowing magma could be observed through gashes within McKenny crater. During February, Fuego underwent mild vulcanian eruptions producing substantial amounts of ash which were interspersed with vaporous ash-poor plumes (Figure 1). Both types of eruption clouds were sampled. Santiguito is a Peléean dome which produced several pyroclastic eruptions each day, some reaching several kilometers above the top of the dome (Figure 2). Decades may elapse between eruptions which produce eruption clouds penetrating the tropopause, and although the composition of relatively small eruption clouds may differ from that of the huge ones, estimates of the composition of the latter based on direct measurements of the composition of the former are more reliable than those based on previously obtained data.

Equipment on the aircraft included (1) a treated filter sampler for determination of relative amounts of SO_2 , HCl, HBr, HF, and SO_4^{2-} , particles and trace elements; (2) a 10-stage piezoelectric cascade impactor for particle size distribution and sampling of particles in the diameter range of 25–0.05 μm ; (3) evacuated stainless steel canisters for gas chromatographic measurements of H_2S , COS, CO_2 , CO, and SO_2 ; (4) an SO_2 correlation spectrometer for the determination of SO_2 fluxes in the plumes by traversing; (5) an automatic 35-mm multi-speed sequence camera for photography of erupting plumes; (6) a flow-through stainless steel gas sampler for H, O, and C isotopic measurements of gases; (7) an inertial navigation sys-

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Fig. 1. Vulcán Fuego erupting on February 27, 1978. A lava flow is occurring to the left of the large rock in the lower center of the picture.

tem for ground and wind velocity determinations; and (8) a gas bubbler sampler for trace element sampling.

The results obtained were presented in a series of papers at the 1978 Fall Meeting of the American Geophysical Union in a special session entitled 'Airborne Sampling of Eruption Clouds of Explosive Volcanoes' and are summarized in abstracts of the meeting [AGU, 1978]. Articles describing the techniques and results in detail are being published separately, largely from the standpoint of volcanology. The purpose of the present article is to discuss the contribution of the results of the flights to our understanding of the impact of violent explosive eruptions on the stratosphere.

RESULTS AND DISCUSSION

The filter samplers, which had been designed by Lazrus and Huebert, each consisted of three filters in series mounted, with separators, in a stainless steel holder. The first was a fluoropore filter to collect particles without appreciable absorption of gases. The other two were Whatman filters impregnated with tetrabutylammonium hydroxide to retain acid gases. Aqueous extracts of the filters were analyzed by Lazrus and Huebert for SO_4^{2-} , particulate Cl^- , SO_2 , HCl , and HF . They were also analyzed for particulate F^- and HF by Smith and Zielinski and for HCl and HBr by Sedlacek.

Some of the results obtained are shown in Table 1 as ratios of mass concentrations. Thermodynamic considerations suggest that most of the erupted sulfur is present in the early

eruption cloud as sulfur dioxide (see, for example, Nordlie [1971]). The canister samples, analyzed by Heidt, indicated orders of magnitude less H_2S and COS than SO_2 , the latter calculated from the filter analyses, although the H_2S and COS values are suspect because of the time (as much as a month) that elapsed between the sample collection and analysis and the likelihood that sulfur compounds partially reacted with the walls of the stainless steel canisters. Also, the eruption clouds had a strong odor of sulfur dioxide. As the eruption clouds cooled and mixed with additional atmospheric oxygen, much of the SO_2 might be expected to be oxidized and hydrated to form H_2SO_4 , possibly catalyzed by volcanic ash. However, although the samples were collected at distances of about 1–30 km from the craters, and under the different conditions of activity, the SO_2 concentrations always greatly exceeded the sulfate concentrations. The particulate chloride-to-sulfate ratios greatly exceed those found in the stratosphere following the injection of volcanic eruption clouds [Cadle, 1972]. They are also different from those found at the volcano Kilauea, in Hawaii, where the sulfate concentration greatly exceeds the concentration of particulate chloride [Cadle et al., 1973]. The aqueous extracts of the fluoropore filters were analyzed for soluble cations by inductively coupled plasma-optical emission spectroscopy. Some of the results are shown in Table 2. The concentrations of water-soluble metallic cations relative to the SO_4^{2-} concentrations were similar to concentra-

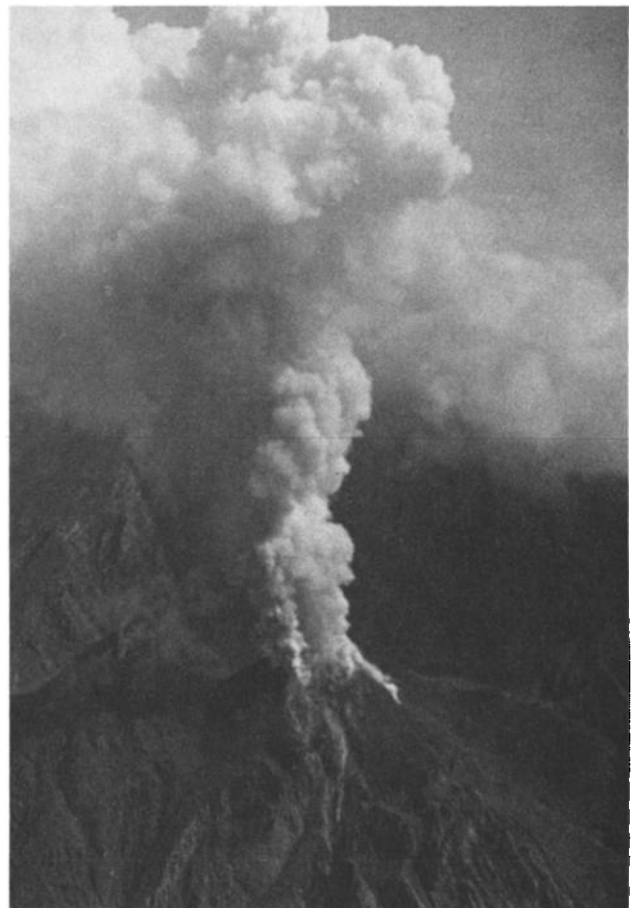


Fig. 2. The Caliente vent of the Santiaguito dome erupting on February 22, 1978. The ash was almost white. Santa Maria volcano, the side of which was blown out by the eruption at the Santiaguito site in 1902, is in the background.

TABLE 1. Partial Results of Analyses of Filters

Volcano	Range of Concentration Ratios (Mass Basis)			
	SO ₂ /HCl	SO ₂ /SO ₄ ²⁻	HCl/HF	Particulate Cl ⁻ / SO ₄ ²⁻
Pacaya	2.2-4.3	26->100	6.7-8.6	0.44-14
Fuego	5.9-14	11->730	6.7-22	0.44-1.9
			6.2, 15*	
Santiaguito	2.2-5.4	9->145	25-81	0.52-0.9

Unless otherwise indicated, analyses were by B. Huebert and A. Lazrus.

*Two samples were analyzed for HF by David Smith and R. A. Zielinski.

tion ratios determined for Arenal (Costa Rica) and Mayon (Philippines) but were much larger than have ever been found in water-soluble material in the stratosphere [Cadle, 1972; Junge and Manson, 1961; Cadle et al., 1969]. If one assumes that ash-water interactions in explosive eruption clouds are equally efficient for removing cations and SO₄²⁻ then the above results considered together strongly support the supposition that most of the sulfur erupted directly into the stratosphere is sulfur dioxide. The much larger proportion of SO₄²⁻ to other water-soluble particulate material in the stratosphere must result from the oxidation of SO₂.

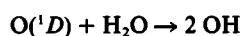
The volcanic SO₂ will deplete the stratosphere of OH until the SO₂ concentration drops to about 4 ppbm (parts per billion by mass). Davis [1974] has shown that the initial reaction is



with a rate constant of about $3 \times 10^{-31} \text{ cm}^6 \text{ s}^{-2}$. Subsequent reactions leading to H₂SO₄ are unknown, but possibly the most important is



The OH is largely formed by



with a rate constant of $7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-2}$ [Hampson and Garvin, 1975]. Then assuming the water vapor concentration to be 10^{13} cm^{-3} , and daytime concentrations of OH and O(¹D) to be $5 \times 10^5 \text{ cm}^{-3}$ (in the absence of much SO₂) and 0.5 cm^{-3} , respectively [Grobecker, 1975], and equating the rates of formation and depletion of OH, the above value of 4 ppbm is obtained. Conversely, higher values of SO₂ put in the equation yield values of OH less than $5 \times 10^5 \text{ cm}^{-3}$. This calculation is, of course, a considerable oversimplification; for example, it neglects other reactions of OH, but it does demonstrate that

volcanic SO₂ can markedly deplete the portion of the stratosphere affected by OH.

The percentage of hydrogen chloride in the fume of the Hawaiian volcanoes is very approximately one-tenth that of sulfur dioxide on a mass basis, and in fumarolic gases from circum-Pacific volcanoes the percentages are nearly equal [Stoiber and Rose, 1973]. Thus one might expect to find almost equal amounts of sulfur compounds and HCl in the stratosphere shortly after eruptions, such as the eruption of Fuego in 1974. Stolarski and Cicerone [1974] suggested that volcanic HCl could influence the stratosphere. However, following the 1974 Fuego eruption the stratospheric HCl concentrations were much smaller (by several orders of magnitude) than might be expected (Cadle et al. [1976], quoting A. L. Lazrus (personal communication, 1975)). Possible explanations for the discrepancy, if it is real, are that falling volcanic ash preferentially removes HCl from the air or that explosive eruptions liberate relatively much less HCl than do fumaroles. A third possible explanation is that torrential rains which often accompany large explosive eruptions, and accompanied the 1974 Fuego eruptions, preferentially removed HCl, which is more soluble in water than is SO₂. The [SO₂]/[HCl] concentration ratios shown in Table 1 were sufficiently close to unity apparently to invalidate the second of these suggestions, especially since the Santiaguito eruptions were quite large. However, these ratios were quite variable.

W. A. Sedlacek (personal communication, 1978), using neutron activation analysis of the samples analyzed colorimetrically for HCl by Lazrus, found comparable amounts of HCl but essentially no HBr above background.

The gas-to-particle ratio for Cl⁻ in the samples of this study was usually considerably less than that for S. However, we do not know whether the particulate Cl⁻ was erupted as HCl which dissolved in condensing droplets of water and H₂SO₄ or was erupted as metal salts in vapor form which later condensed. Judging from the energy dispersive X ray analysis

TABLE 2. Concentrations of SO₄²⁻ and Various Water-Soluble Particulate Cations in Volcanic Fume

Volcano	Cation											
	SO ₄ ²⁻	Ca	Cd	Cu	Fe	Mg	Mn	Na	Pb	Sr	V	Zn
Pacaya	0.4	34	0.03		9.0	17	0.3	2.0		0.05	1.0	3.9
Fuego	4.0	240	0.06	0.53	180	150	3.8	46	0.3	1.9	0.5	1.2
Fuego	<17	64		3.4	36	29	0.6		1.9	0.2	5.2	2.1
Fuego	3	30	0	0.2	22	19	0.4	2.9		0.2	0.3	0.1
Fuego	16	100	0.2	0.4	92	79	1.7	15		0.8	0.6	0.9
Fuego	48	280	0.2	0.6	160	130	3.1	52	4.0	2.0	0.3	1.4
Santiaguito	49	100	0.1	0.2	14	9.0	0.5	20	0.1	0.5	0.3	0.8
Santiaguito	22	28	0.3	0.2	5.0	3.0	0.2	5.9		0.2	0.7	1.7

Values are expressed as parts per billion by mass. Corrected for blank. Only a few results which are markedly above the blank are presented. Analysis for cations was by D. Smith and R. A. Zielinski.

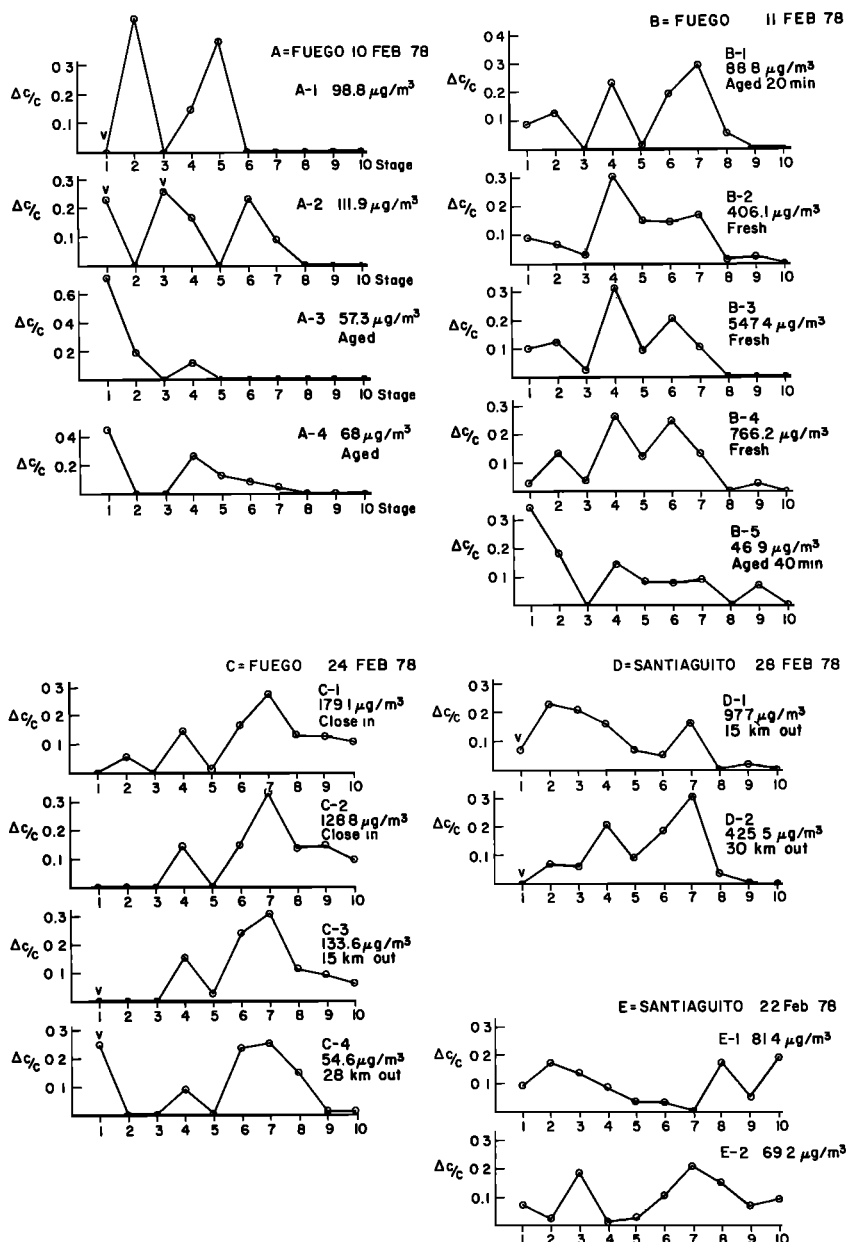


Fig. 3. Size distributions obtained with the cascade impactor for Fuego and Santiago eruption clouds. The symbol v indicates that an initially higher signal decayed because volatile particles collected on that stage. $\Delta C/C$ on the ordinate represents the fraction of the total concentration which collected on a particular stage. The total concentration for each plot is given at the upper right. The 50% cutoff diameter for particles with density $2 \text{ g}/\text{cc}$ accumulating on each stage from 1–10 is 25, 12, 6.4, 3.2, 1.6, 0.8, 0.4, 0.2, 0.1, and $0.05 \mu\text{m}$, respectively.

(EDXRA) analyses of particles collected with the impactors [Rose *et al.*, 1979a] much of it was erupted in the latter form. Additional measurements of $[\text{SO}_2]/[\text{HCl}]$ concentration ratios in the stratosphere following stratosphere-penetrating eruptions will be needed to determine whether HCl is usually preferentially removed from the eruption clouds. Since such eruptions occur sporadically, it may be many years before this uncertainty is resolved.

The 10-stage impactor collected particles on a piezoelectric crystal at each stage. The impactor was mounted near the end of one aircraft wing, and the readout and printout of the mass of particles collected on each stage, as well as controls, were within the plane cabin. This system, called the QCM cascade impactor, was furnished by Chuan and Woods. Size distribu-

tions could be obtained for a number of samples on each flight [Chuan, 1976]. The diameters collected with 50% efficiency were 25, 12, 6.4, 3.2, 1.6, 0.8, 0.4, 0.2, 0.1, and $0.05 \mu\text{m}$ for stages 1–10, respectively, and assuming a particle density of $2 \text{ g}/\text{cm}^3$.

Particles were also collected with a single-stage hand-held impactor [Cadle, 1975b, Figures 2–29 and 2–30]. Collection was on Formvar films on electron microscope grids.

Size distributions of the particles in the Fuego and Santiago eruption clouds are shown in Figure 3. The size distributions were bimodal or trimodal, and possible explanations for the multimodal distributions are discussed by Rose *et al.* [1979a].

Only particles smaller than about $2 \mu\text{m}$ in diameter will

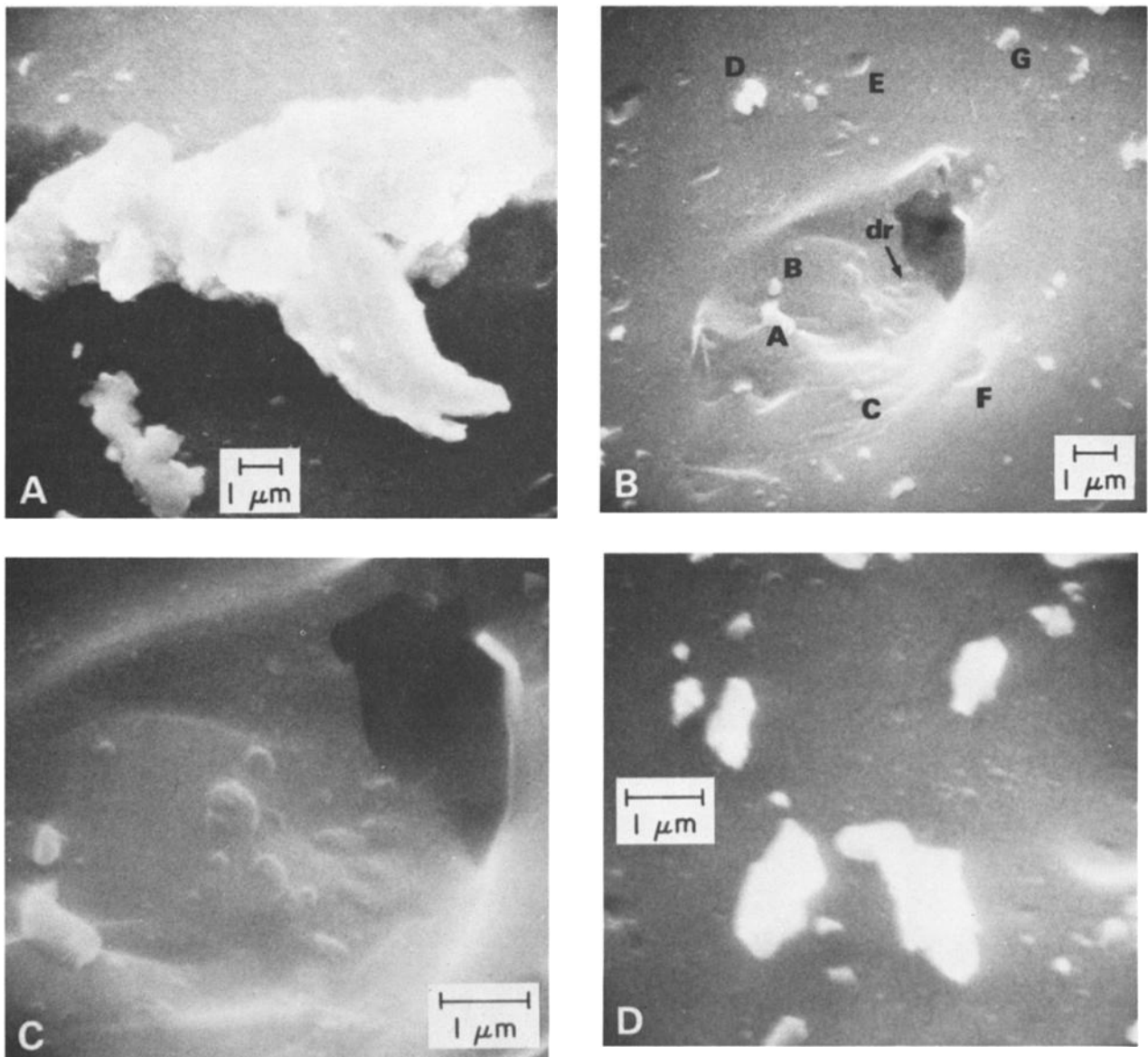


Fig. 4. Scanning electron micrographs of particles collected with the single-stage impactor from Pacaya fume. The EDXRA results indicated are as follows. (a) The large particle contained large amounts of Zn and Al. (b) A was basaltic glass; B, C, D, and G were plagioclase; E was nonemitting; and F was a sulfur-containing droplet, as was the droplet marked dr. (c) An enlargement of the center of Figure 4b. The dark region was probably a tear in the Formvar film. (d) The four larger angular fragments were plagioclase.

have much effect in the stratosphere for very long time periods because of the relatively rapid settling rate of larger particles. These smaller particles were collected on stages 5–10 (see, for example, Mossop [1964]). One of the modes in the particle size distributions usually appeared in this range (1.6–0.05 μm diameter).

It is important to realize that the particles collected with the cascade impactor represent the fine 'tail' of a size distribution that is substantially enriched in the clouds because of fallout of the mostly larger particles. Particles could often be observed streaming down from the eruption clouds.

Electron micrographs of particles collected with the single-stage impactor are shown in Figures 4–6. Judging from the theory of Ranz and Wong [1952] the theoretical diameter for 50% collection efficiency for a pressure drop of about 0.5 atm across the jet at 760 torr and 273 K is about 0.15 μm assuming

a particle density of 2 g/cm^{-3} . Figure 4 consists of four scanning electron micrographs of particles collected from the Pacaya plume. The particles were mainly droplets which EDXRA analysis showed were rich in sulfur and were probably impure H_2SO_4 , but some particles were volcanic ash and an occasional unusual crystal, such as the large one in Figure 4a which was rich in Al and Zn. The analyses also showed that many of the particles consisted of plagioclase fragments 1 μm or smaller in diameter and small fragments of basaltic glass.

The scanning electron micrographs of Figure 5 were of particles collected from Fuego when it was erupting large puffs of ash every few minutes. The particles were collected 20–30 km from the vent and corresponded roughly to the 'aged' samples in Figure 3. The EDXRA analyses were interpreted as revealing some impure sulfuric acid droplets, fragments of plagioclase, and glass.

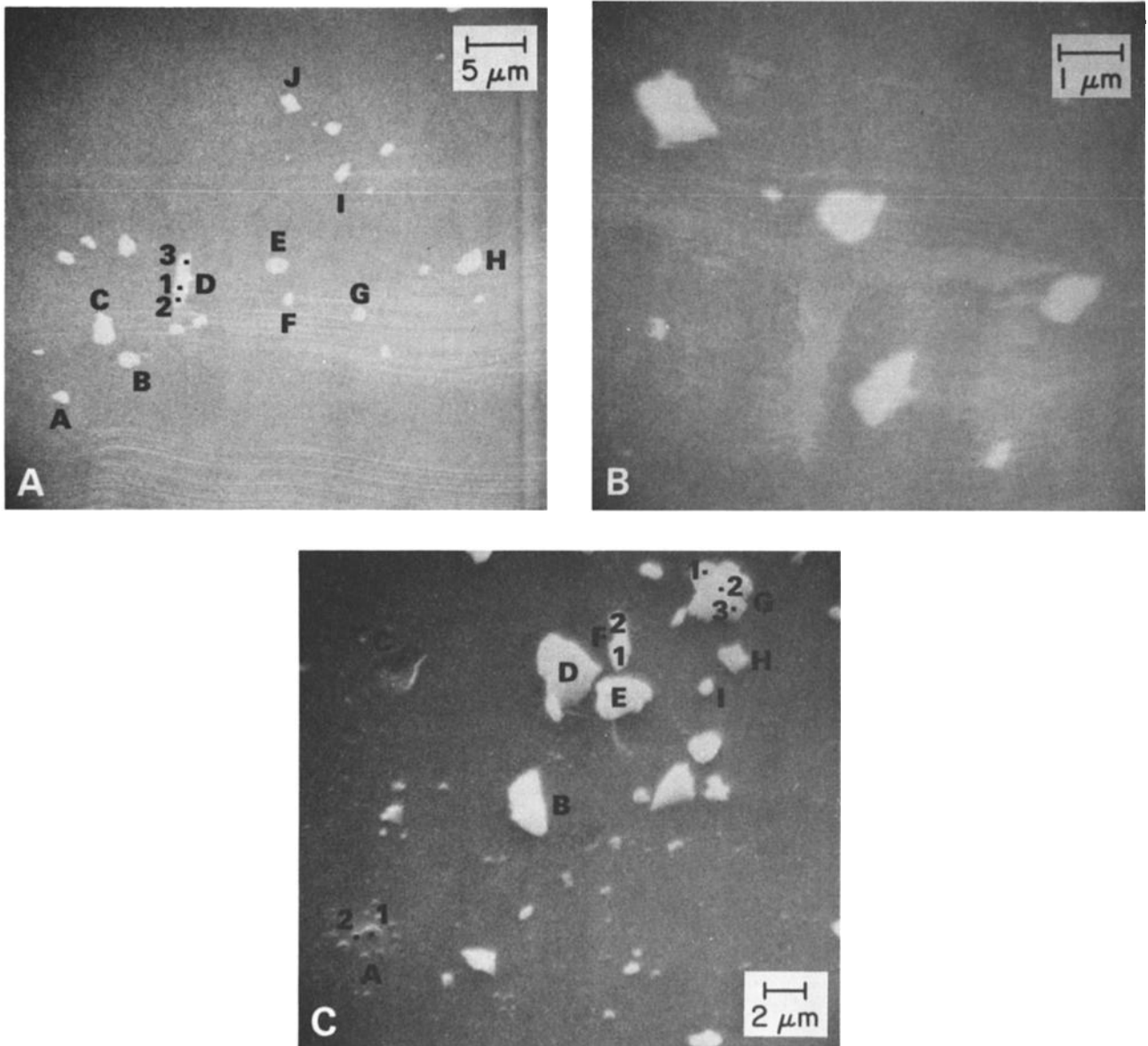


Fig. 5. Scanning electron micrographs of particles collected with the single-stage impactor from Fuego eruption fume on February 11, 1978. The EDXRA results indicated are as follows. (a) A, B, I, and J were plagioclase; C was glass; D-1 and D-2 exhibited a hybrid pattern of plagioclase and glass with Na, Mg, Al, Si, Fe, Ca, and traces of S and Cl which may have been an acid coating; D-3 was the same as D-1 and D-2 but had a higher proportion of Ca and Al; E contained Mg, Al, Si, Se, Fe, S, and Cl; F contained Ca and Fe with small amounts of Si, Al, S, and Ti; G was glass; and H was probably mainly glass. (b) The composition of the particles was not determined. (c) These particles were similar to (a), except for A-1 and A-2, which were sulfuric acid droplets, and C, which showed no EDXRA pattern.

Figure 6 consists of four transmission electron micrographs of particles collected from Santiaguito eruption clouds, showing angular silicate particles and droplets that were probably impure sulfuric acid. Note that the silicate particles in Figure 6c have droplets clinging to them which may have been intercepted by the larger particles or in some cases may have condensed on them. Figures 6a and 6d were obtained on February 22 (see Figure 3 for size distributions), and Figures 6b and 6c were obtained on March 1.

Scanning electron micrographs and EDXRA patterns were also prepared of the eruption cloud particles collected on the various stages of the cascade impactor from Santiaguito on February 28 and from Fuego on February 11. These are discussed in detail by Rose *et al.* [1979a]. The Santiaguito sam-

ples on stages 1–5, cutoffs $>1\text{-}\mu\text{m}$ diameter, consisted mainly of two kinds of particles. One type consisted of angular silicate particles of rhyolitic composition, like the groundmass of Santiaguito lavas. The other type consisted of droplets, probably impure sulfuric acid, which were much smaller than the cutoff sizes for the stages. These droplets may have been knocked loose from the silicate particles upon impact with the impactor surface. The particles collected on stages 6–10 were markedly different from those collected on 1–5. Crystal fragments of plagioclase and magnetite with liquid coatings predominated, and in stages 7–10 the fragments protruded out of a sea of condensed droplets. Similar differences between the particles collected from Fuego fume on stages 1–5 and 6–10 were observed.

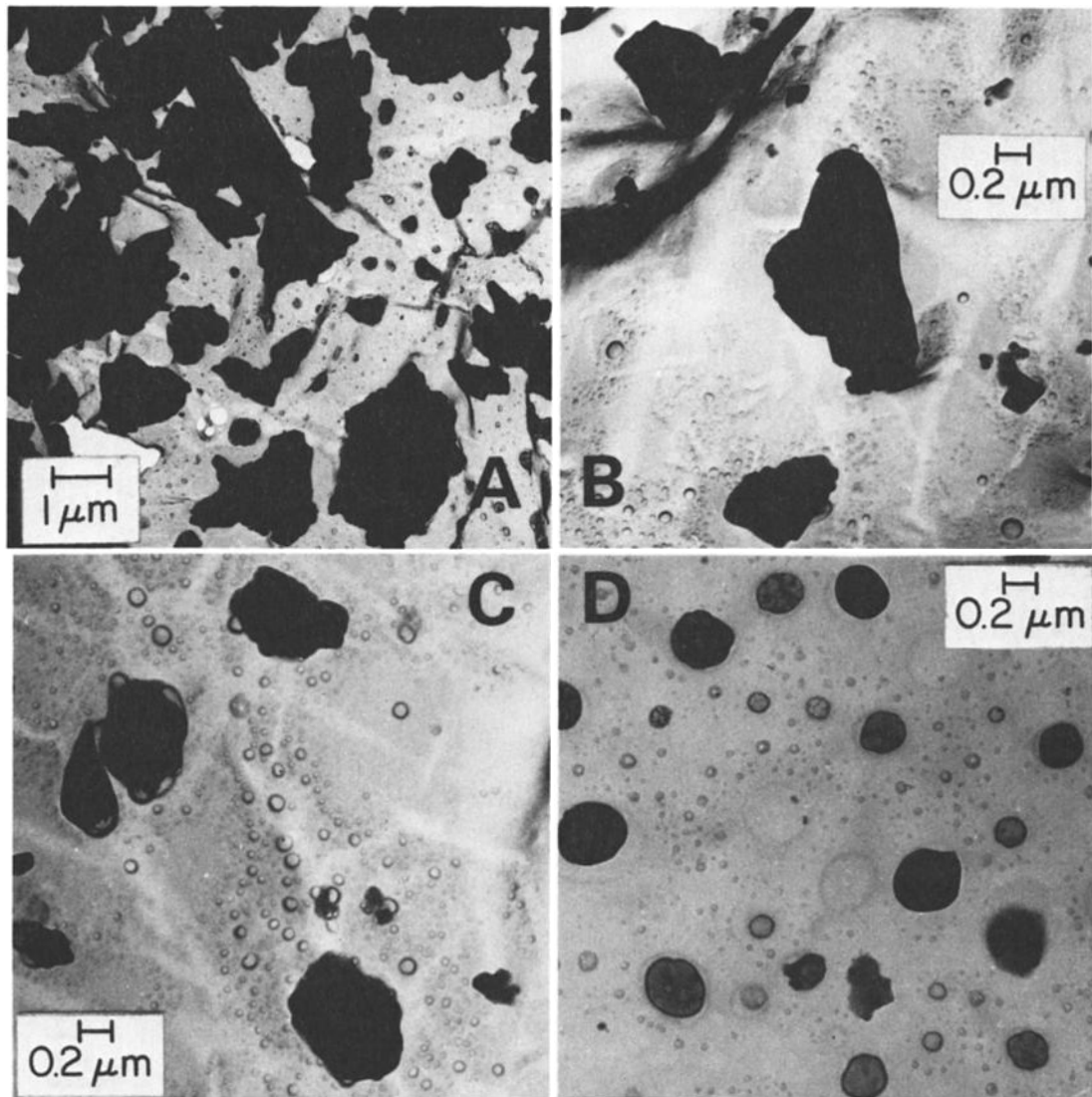


Fig. 6. Transmission electron micrograph of particles collected with the single-stage impactor from Santiaguito eruption fume on September 22 (a and d) and on March 1 (b and c).

The large percentage of crystal fragments among the finest particles collected suggests that a magma that contains a high percentage of crystals may produce smaller ash particles (which will remain in the air for a long time) than an essentially noncrystalline magma.

The sources of carbonyl sulfide (COS) are of interest with regard to the particulate content of the atmosphere, especially of the stratosphere, because of the recent suggestion that COS is the main source of sulfuric acid droplets in the stratosphere during periods when there is little extremely explosive volcanic activity. COS may have a long tropospheric residence time [Crutzen, 1976]. However, it now seems likely that the main 'sink' for COS is reaction in the troposphere with OH and that the residence time is about 1.5 years [Kurylo, 1978]. COS, H₂S, and CO₂ concentrations along with concentrations of a number of other compounds were measured by gas chromatography of the gases in the canisters. Some of the COS and H₂S may have been lost by adsorption on the canister walls or by the sampling procedure, so we are not presenting actual concentrations. A calculation based on the largest [COS]/[CO₂] ratio and using a residence time of 1.5 years,

corrected for the concentrations in the unperturbed atmosphere, suggests that the volcanic source of COS is trivial. The calculation assumed that the undiluted fume contained 20% by mass of CO₂. Additional measurements are needed in which wall losses are avoided. Rose *et al.* [1979b] concluded that the more explosive ash-laden clouds sampled in Guatemala had higher sulfur contents on the basis of both the SO₂/HCl concentration ratios and on the COS and H₂S results.

Stoiber and Bratton reported at the AGU meeting mentioned earlier that their measurements with the correlation spectrometer and wind velocity data obtained with the airplane's inertial navigation system yielded emissions of SO₂ from each of the three volcanoes of 300–1500 metric tons per day. It is interesting to note that assuming the volcanoes emitted an average of 1000 metric tons each per day, this rate would amount to 1×10^6 metric tons per year for these three volcanoes as compared to an estimate by Cadle [1975a] of the average global emission rate of SO₂ by volcanic eruptions of 7.8×10^6 tons. Another estimate, 1×10^7 metric tons of SO₂ per year by Stoiber and Jepsen [1973], was based on correlation spectrometer measurements. These estimates if correct in-

dicates that these three volcanoes are supplying one-eighth to one-tenth of the annual volcanic SO₂ production. The estimates are therefore probably too low, perhaps by as much as an order of magnitude.

CONCLUSIONS

The following are tentative conclusions based on measurements of small- to medium-size explosive eruption clouds at two volcanoes and fume at one strongly fuming volcano. As was stated earlier, extrapolating to huge eruptions, such as that of Agung in 1963, may lead to erroneous conclusions, but these are more likely to be correct than previous conclusions based on measurements at fumaroles or the fume from Hawaiian-type eruptions.

1. Most of the sulfur entering the stratosphere from very explosive eruptions is in the form of sulfur dioxide which, by reaction with OH, may deplete the portion of the stratosphere affected by OH for many months and produce sulfuric acid droplets which affect the earth's radiation balance.

2. Explosive eruptions introduce almost as much hydrogen chloride as sulfur dioxide to the atmosphere although the relative amounts are quite variable. Possibly, HCl is largely removed by rain accompanying many large eruptions.

3. Magmas containing a large percentage of crystals probably produce a much larger proportion of very fine particles that remain in the stratosphere for many months than magmas containing small percentages of crystals.

4. Volcanoes probably contribute insignificantly to the carbonyl sulfide content of the atmosphere, but more data on residence times and better data on volcanic emissions of COS are needed.

5. A two-dimensional dynamic model of the transport of tracers in the stratosphere has been applied to the global scale dispersion of the volcanic clouds injected into the stratosphere by violent eruptions [Cadle *et al.*, 1976, 1977]. The model does not include chemical reactions and predicts the dispersion of only that ash which is sufficiently fine that its settling rate can be neglected. The results of the work described here demonstrate that refinements of such a model should include the conversion of SO₂ to H₂SO₄ droplets, which may require a year for nearly complete conversion, and the crystallinity of the erupted magma.

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