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Sulfur Dioxide and Particles in Quiescent Volcanic Plumes From Poás, Arenal, and Colima Volcanos, Costa Rica and Mexico

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Measurements of SO₂ emission rates and concentrations and of particle distribution, size, shape, and composition were made in quiescent volcanic plumes emitted into the troposphere from Poás and Arenal volcanos, Costa Rica, and Colima volcano, Mexico. SO₂ emission rates were 700 ± 180 metric tons per day (t/d) for Poás, 210 ± 30 t/d for Arenal, and 320 ± 50 t/d for Colima. The concentrations of SO₂ calculated from the COSPEC/lidar data were 5–380 ppb. Concentrations of SO₂ measured directly by flame photometry were 10–250 ppb. Particles collected in the plumes with a quartz crystal microbalance impactor were mostly less than 3 μm in diameter and consisted of droplets of dilute sulfur-bearing solutions and minor amounts of larger silicate particles coated with a sulfur-bearing film or crust. Total particle concentrations were 4.7 $\mu\text{g}/\text{m}^3$ for Poás and 18.8 $\mu\text{g}/\text{m}^3$ for Colima. Comparison of concentrations of SO₂ in the plumes with gas samples collected at fumaroles on the ground suggests that the plumes are diluted by the atmosphere by factors of up to 10⁵.

INTRODUCTION

Nature seems to have set up excruciating obstacles to progress ranging from personal hazard to capricious and irreproducible behavior. Most problems have required multidisciplinary approaches for significant progress.

A. T. Anderson (1975)

Explosive volcanic eruptions of the type that contribute gas and ash to the stratosphere are relatively rare events, occurring on average between 1 and 3 times per year [Newhall and Self, 1982]. Much more common are the continuous emissions of gas, frequently with minor ash, to the troposphere that accompany nonexplosive eruptions or that occur during quiet periods at active volcanos. Recent evaluations [Berresheim and Jaeschke, 1983; Stoiber et al., 1983] indicate that quiescent plumes make up the majority of the global volcanic flux of sulfur and other gases to the atmosphere. These gases are mostly water with minor amounts of CO₂, H₂, SO₂, and H₂S. Sulfur gases of volcanic origin appear to exert an important influence on the chemistry of the atmosphere and the earth's climate, possibly overshadowing the effects of eruption clouds, which carry large amounts of solid ejecta [Newell and Deepak, 1982; Rampino and Self, 1982; Sigurdsson, 1982]. To assess the impact and significance of the volcanic contribution to the atmospheric sulfur reservoir, it is important to identify the precursory sulfur gases as well as the rates at which, and physical conditions under which, these gases enter the atmosphere.

The fate of SO₂ and other sulfur gases in tropospheric plumes is of wider societal concern as well. Sulfur dioxide is acknowledged as a principal contributor to the problem of acid precipitation. Volcanos, the primary natural source of SO₂, account for approximately 10% of the total global production of sulfur dioxide [Berresheim and Jaeschke, 1983]. Also, the emission rates of SO₂ in volcanic plumes are measured regularly at several volcanos, such as Mount St. Helens,

Washington [Casadevall et al., 1981, 1983]; Kilauea volcano, Hawaii; Mount Etna, Italy; and Merapi, Indonesia, and these rates provide information for monitoring volcanic activity. It becomes especially important, therefore, to identify processes which might affect the SO₂ in volcanic plumes.

In this paper we report the results of airborne and ground-based studies made in February 1982 of quiescent volcanic plumes from Poás and Arenal volcanos, Costa Rica, and Colima volcano, Mexico (Figure 1). These results include the first, nearly simultaneous airborne measurements in the same volcanic plumes of (1) sulfur dioxide emission rates; (2) sulfur gas concentrations; (3) particle chemistry, distribution, size, and shape; and (4) plume structure. The measurements were part of the RAVE (Research on Atmospheric Volcanic Emissions) experiment to assess the impact of volcanic emissions on the atmosphere [Friend et al., 1982].

During this mission, the much-publicized "mystery cloud" of aerosols in the stratosphere was detected by lidar measurements made during the flight between Wallops Island, Virginia, and San Jose, Costa Rica. The latitudinal expanse of the layer along with the characteristic vertical profile, measured by lidar, indicates it most likely originated from a volcanic source. Also during this mission, Telica volcano in Nicaragua erupted explosively on February 12, 14, 15, and 19, 1982. The maximum altitude of the Telica plumes was estimated at 4.3 km (SEAN Bulletin, 7(2) 1982), well below the tropopause. Neither the "mystery cloud" nor the Telica activity interfered with measurements during this mission. El Chichon volcano in Mexico did not erupt until March 28, 1982.

DESCRIPTIONS OF VOLCANIC PLUMES

The gases that form the volcanic plumes first entered the atmosphere from fumaroles located in the craters of the three volcanos. The quiescent plumes remained in the troposphere below 4-km altitude. Air and ground observations were made at Poás and Arenal, while observations of Colima were made only from the air.

Poás Volcano, Costa Rica

Poás volcano (elevation 2420 m) has a broad shield form and is located in central Costa Rica at the western edge of the Central Volcanic Range (10°11'N, 84°13'W) (Figure 1). Poás has had continuous, strong fumarolic activity since first observed in 1828. After 36 years of relative quiet, Poás resumed activity with a series of eruptions between 1952 and 1956.

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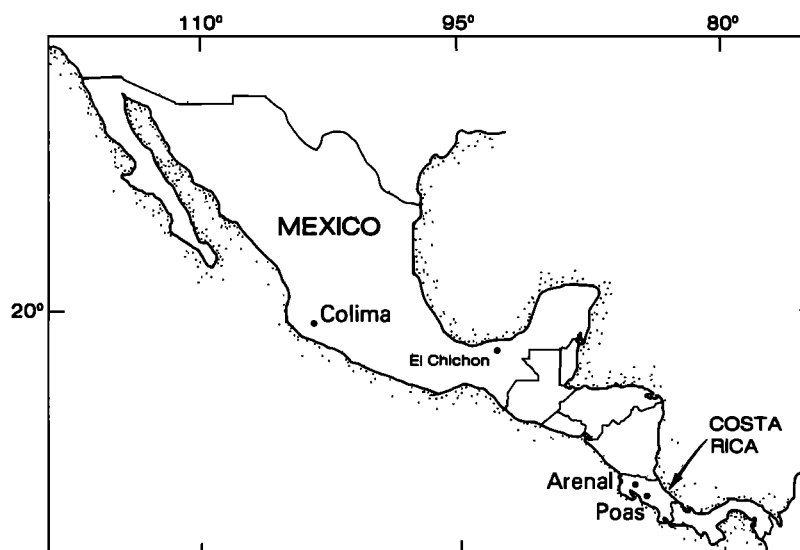


Fig. 1. Map showing locations of Arenal, Poás, and Colima volcanos, Costa Rica and Mexico. El Chichon volcano, located for reference, did not erupt until March 1982.

Mild Strombolian activity in 1954 and 1955 built a 40-m-high cone of basaltic cinder and lava on the floor of the main crater (elevation 2300 m). A crater lake formed in 1965. In February 1982 this lake had a temperature of 48°C and a pH of 0.1; abundant particles of elemental sulfur were suspended in the water and floated on the surface.

Activity through 1980 included vigorous fumarolic activity accompanied by minor phreatic eruptions; these eruptions also produced pyroclasts of nearly pure sulfur [Bennett and Raccichini, 1978; Francis *et al.*, 1980]. A similar occurrence was reported by Ohashi [1919] from Kusatsu-Shirane volcano in Japan. In both cases the authors suggested that a body of liquid sulfur existed below the lake prior to eruption. The liquid sulfur was apparently quenched against the lake water at the time of eruption.

The mass of liquid sulfur under Poás may be of fumarolic origin or from precipitated sulfur that remelted and collected as a liquid within the crater. Whitney and Stormer [1982] have shown that many magmas of intermediate and silicic composition have intensive parameters that make it likely for a sulfur liquid to form, but such liquid bodies have not been observed by petrologists. The sulfur within the Poás crater lake may also represent a sulfur liquid that had separated from the silicate magma at some depth and migrated upward.

Virtually all gas emissions at Poás come from fumaroles located on the east side of the 1954–1955 tuff cone immediately adjacent to the lake. The fumaroles occur along several parallel fractures that cover an area of a few hundred square meters. High-temperature fumaroles (up to 940°C) were reported at Poás for the first time in January 1981. (J. Barquero and E. Malavassi, written communication, 1982), and rock in the interior of the fumaroles was incandescent at a temperature of 883° in February 1982. Gases from these fumaroles are largely water, with lesser amounts of carbon dioxide, sulfur dioxide, and hydrogen (Table 1).

Emissions from the fumaroles form a large whitish gas plume (Figure 2a), which is usually carried through a broad gap between ridges at the southwest edge of the crater. Local wind effects and topography combine to channel the plume below the elevation of the peak and out into a wide valley. The luxuriant tropical vegetation surrounding Poás is missing

from the upper reaches of this valley because of the continual fumigation by the plume. On February 17, 1982, the winds at Poás were light and variable (2.4–4.0 m s⁻¹), and the axis of the plume wandered slightly. The skies in the vicinity of the volcano were cloud free during the morning hours when measurements were made.

Arenal Volcano, Costa Rica

Arenal volcano (elevation 1633 m) is located at the eastern end of the Guanacaste Volcanic Range in northwestern Costa Rica (10°27.8'N, 84°42.3'W) (Figure 1). Following minor activity in the 16th century, no activity was recorded at Arenal until July 1968, when an early explosive phase was followed by eruption of lava flows of basaltic andesite composition [Malavassi *et al.*, 1982; Wadge, 1983]. In February 1982 the 38th lava flow in this eruption was descending to the southwest for approximately 1 km from the active crater below the

TABLE 1. Chemistry of Gas Emissions at Poás and Arenal, Costa Rica

Gas	1979*	Poás 82-5†	82-3‡	Arenal*
H ₂ O	95	ND	79.5	94
Gas Composition Calculated on a Water-Free Basis				
H ₂	15.4	26.5	9.1	8
CO ₂	23.3	32	51.0	50
CO	0.15	1.3	<1.0	0.27
CH ₄	0.006	<0.001	<0.006	0.12
SO ₂	61.2	40.5	34.4	37
H ₂ S	0.2	<0.01	34.4	0.9
HCl	ND	ND	3.2	ND
HF	ND	ND	0.5	ND
O ₂ + N ₂ + Ar	¶	¶	1.9	¶
Collection temperature, °C	940	870	870	930–954

All emissions given in volume percent; ND, not determined.

*Cheminee *et al.*, 1981.

†Flow-thru bottle; H₂O not determined; analysis by L. P. Greenland.

‡Evacuated bottle partially filled with NaOH; total sulfur determined as H₂S; analysis by D. Sheppard.

¶Calculated on an air-free basis.

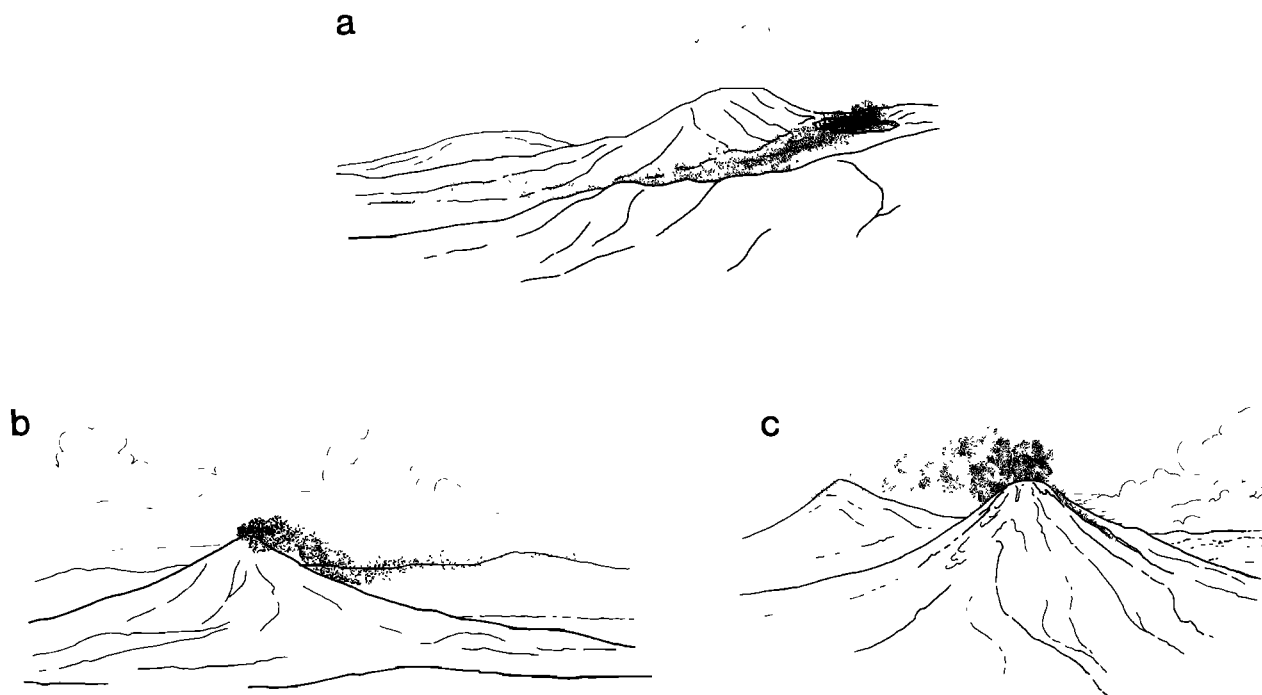


Fig. 2. Interpretive line drawings of volcanic plumes (stippled areas): (a) View of Poás from east showing summit caldera and channelized flow of plume between ridges. (b) View of Arenal from southeast showing looping of plume as a result of thermal instability of atmosphere. (c) View of Colima from southeast showing thin plume being carried toward the peak Nevado de Colima.

summit. Accompanying this extrusion of lava was a whitish, translucent gas plume that originated from both the active crater and the summit crater (Figure 2b). The gases that form the plume originate from high-temperature fumaroles whose major sulfur gas is SO₂ (Table 1) [Cheminee et al., 1981]. On February 15 and 16 the sky was cloudy, partially obscuring the peak and the plume. On the 16th the plume displayed looping behavior (Figure 2b), indicating thermal instability of the atmosphere.

Colima Volcano, Mexico

Colima volcano (elevation 3960 m) is located at the western end of the Mexican Volcanic Belt (19°30.7'N, 103°37'W) (Figure 1) and has been Mexico's most active volcano over the past 400 years [Luhr, 1981]. The present activity began with the eruption of andesite lava flows, first in 1961–1962 and again in 1975–1976 [Luhr and Carmichael, 1980]. In early December 1981 a third lava flow began flowing from the summit crater (J. Luhr, written communication, 1982) and had moved down the south face of the volcano for about 1 km by February 1982. On February 20 a translucent greyish-white gas plume emanated from the north side of the crater (Figure 2c) and disappeared quickly because of evaporation in the dry air and mixing as it was dispersed downwind. Directional shear caused by variation in wind direction with altitude strongly affected the geometry of the plume on February 20 to produce a wide, thin plume. The skies around Colima were cloud free during these measurements.

METHODS AND RESULTS

All measurements were made from a Lockheed Electra aircraft from the NASA facility at Wallops Island, Virginia. Measurements were made on February 16 and 17, 1982, at Poás; February 15, 16, and 19 at Arenal; and February 19

and 20 at Colima. The measurements at each volcano were made in a systematic sequence. First, we determined the position and bottom surface of the plume by flying beneath the plume to make measurements of sulfur dioxide emission rates and plume structure. These traverses were made at distances of 1 to 20 km from the plume source as flying conditions permitted. Next, the aircraft climbed to penetrate the plume to measure the concentrations of sulfur gas and obtain high-volume filter samples and impactor samples. The following sections describe the measurement techniques and summarize the results of measurements made during the mission.

Sulfur Dioxide Emission Rates

The emission rates of sulfur dioxide were measured with a correlation spectrometer (COSPEC). The COSPEC has been used for ground-based measurements of smokestack plumes [Millan et al., 1976] and volcanic plumes [Stoiber and Jepsen, 1973]. The technique also has been adapted for airborne measurements at volcanos in Central America [Cadle et al., 1979]; Soufriere, St. Vincent, West Indies [Hoff and Gallant, 1980]; Mount St. Helens [Casadevall et al., 1981, 1983], Washington, and Mt. Etna, Italy (J. Carbonnelle, written communication, 1982).

The COSPEC measures the path-length concentration (ppm/m) of SO₂ in a cross section of the plume by analyzing incident ultraviolet radiation for absorption by SO₂. Traverses were made by flying beneath and perpendicular to the plume. The plume width (m) is calculated from the width of the part of the chart recorder trace indicating the presence of SO₂ and the aircraft speed. The aircraft speed and the plume velocity were determined by using the on-board inertial navigation system and are accurate to ±10% of the reported value (R. Navarro, written communication, 1982). The product of the path-length concentration, the plume width, and the wind ve-

locity gives the emission rate of SO₂ (ppm/m³/s⁻¹) and is reported as metric tons per day (t/d). The method and an analysis of the uncertainty are described in *Millan and Hoff* [1978], *Hoff and Millan* [1981], and *Casadevall et al.* [1981]. The plume velocity contributes the major uncertainty of the measurement. The reported values for the sulfur dioxide emission rate are the mean value of at least four traverses (Table 2). SO₂ emission rates at Poás were 810 ± 420 t/d on February 16 and 700 ± 180 t/d on February 17; at Arenal 210 ± 30 t/d on February 16 and 160 ± 35 t/d on February 19; and at Colima 320 ± 50 t/d on February 20.

Plume Structure

Method of study. The structure of the plume was studied by the combination of simultaneous COSPEC and lidar measurements. The lidar (light distance and ranging) technique, previously used for airborne measurements of the volcanic plume of Soufriere volcano, St. Vincent [*Fuller et al.*, 1982], uses the backscatter from a vertically directed laser beam to measure the distribution and density of particles in the plume. Cloud-free conditions permitted successful operation of the lidar on February 17 at Poás and February 20 at Colima.

The airborne lidar used in this study is an up-looking, low-power system operating at 1.06 μm and at a 10 pulses per second (pps) repetition rate. It consisted of a Nd:Yag laser transmitter, a 20-cm cassegrain telescope receiver, a silicon detector with log amplifier, a computer controller, and a high-speed data acquisition system with on-line plotting capability. The system used a 41-cm-diameter window in the roof along the centerline of the aircraft. A short intense laser pulse is

transmitted into the atmosphere through the window, and the collinear telescope receiver collects the backscattered light as the laser pulse propagates through the atmosphere. The backscattered energy is a function of the molecular and particulate density in the scattering volume. The light is then directed onto a silicon photodiode detector in series with a log amplifier to reduce the saturation effect of the strong near-field signal. The analog output is measured as a function of time and can therefore be expressed as a function of altitude. The signal is converted to digital data and stored on magnetic tape. The data then can be recalled through the graphics unit, and individual, vertically resolved profiles can be plotted as shown in Figure 3.

The lidar measurements were used to define the width and thickness of the volcanic plume from a series of vertical profiles obtained while flying under the plume and perpendicular to the direction of plume flow. The enhancement in the signal level of each vertical profile, due primarily to particulates, is used to define the volcanic plume. Figure 3a is a series of altitude-resolved lidar profiles plotted as 1-s intervals; each profile is an average of 10 laser shots. Figure 3b is an intensity-modulated display of each profile, indicating the cross-section density of the plume. In this plot the density of each vertical line is proportional to the respective scattering ratio values of the altitude-resolved profiles in Figure 3a. When these lines are plotted as a series (Figure 3b), they map out the cross section of the plume along the flight path. Figure 3c shows the integrated values of each profile, producing a plot of vertically integrated scattering across the plume.

Results. The plume at Colima ranged from 2 to 5 km in width and from 0.8 to 1.1 km in thickness (Figure 4a, b). The Poás plume ranged from 10 to 17 km in width and 0.9 to 1 km in thickness. True widths of the Poás plume were probably less than the measured width, however, since true cross sections were difficult to measure as a result of meandering of the plume. The shape and dimensions of the plume also might have been influenced by the higher wind speeds at Colima (5–6 m/s) versus Poás (3–4 m/s) as well as by the larger flux of gas and particles from Poás. Also, Colima is a taller volcano and not surrounded by topography as rugged as that at Poás (Figure 2a, c). This allows for freer dispersion and flow of the plume and minimizes local eddy effects. The plumes at both Poás and Colima were thickest at their centers and tapered at their edges and, in this respect, were similar to plumes mapped at Mount Baker [*Radke et al.*, 1976] and Mount St. Helens [*Casadevall et al.*, 1981; *Harris et al.*, 1981], Washington, and at Mt. Etna (J. Carbonnelle, written communication, 1982) Italy. Downwind dispersion caused the plumes to expand while being diluted. The maximum column densities of SO₂ measured by COSPEC decreased as the plume widened (Figure 4c, d), while the calculated SO₂ emission rates remained nearly constant. This is consistent with mass conservation of SO₂ in the plume, at least to distances of 20 km from the volcano.

The coincident shapes and widths (Figure 4a) of the lidar and COSPEC traces suggest a uniform distribution of gas and particles in the plume. In several traverses at Colima where the width of the COSPEC (SO₂ gas) plume exceeded the lidar (particle) plume the difference may have been due to evaporation of water droplets near the edges of the plume. We noted that the plume became less visible as it was carried downwind, and we infer that this loss of visibility was due to gradual evaporation of water from the edge of the plume. The wider

TABLE 2. SO₂ Emission Rates

	Poás	Arenal	Colima
February 16	550 320 710 1100 1350 810 ± 420 n = 5	225 200 250 190 240 210 ± 30 n = 5	
February 17	480 920 600 850 (1840*) 700 (2100*) 700 ± 180 n = 5		
February 19		200 140 140 160 ± 35 n = 3	230
February 20			260 310 310 280 290 335 360 410 320 ± 50 n = 8

*Emission rates in metric tons per day. Portion of traverse included flying parallel to plume.

LIDAR TRAVERSE OF COLIMA VOLCANIC PLUME

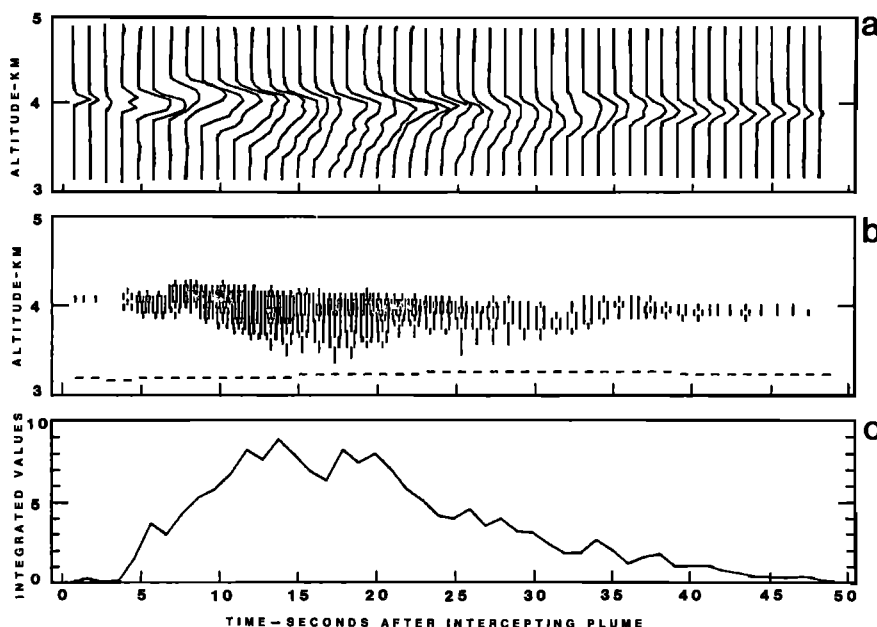


Fig. 3. Lidar data from traverse at Colima, February 20, 1982: (a) Altitude-resolved profiles plotted at 1-s intervals as the plane flew beneath the plume; each profile is an average of 10 laser shots. (b) Intensity-modulated plot of each vertical profile of Figure 3a indicating the cross-section density of the plume. The dashed line beneath the plume is the aircraft altitude at each lidar measurement point. (c) Plot showing integrated values of each vertical profile of Figure 3a across the plume.

plume detected by the COSPEC may also be due to the wider viewing field of the COSPEC beam. At the edge of the plume the field of view includes a portion of plume-free air, while the signal recorded is an average of the entire view field.

Calculated concentrations of sulfur gases. Assuming that the SO₂ and light-scattering particles are well mixed within the plume, we calculated the SO₂ concentration in the plume by dividing the path-length concentration of SO₂ measured by COSPEC by the thickness of the plume determined by the lidar measurements. Table 3 presents an example of calculations made for one of the five traverses for the Colima plume on February 20. The calculated values of SO₂ concentration in the Colima plume range from 5 to 380 ppbv. For the Poás plume on February 17 the calculated values range from 20 to 300 ppbv. By comparison the concentration of sulfur dioxide in the clean troposphere normally ranges from 0.09 to 0.15 ppb [Maroulis *et al.*, 1980].

Direct Measurement of Sulfur Gas Concentrations

A modified Meloy 285 flame photometric detector (FPD) was used for continuous total gaseous sulfur determinations in the plume. A Constant Absolute Pressure Inlet System (CAPIN) operated at a constant pressure of 720-mm Hg and, specially constructed for control of burner block conditions (pressure, temperature, mass flows, and gas ratios), provided instrumental response independent of aircraft altitude. The CAPIN system is designed for internal, in-flight sample calibration by using compressed gas cylinder and permeation tubes and sample dilution modes. Without the strict regulation of the burner block pressure provided by the CAPIN, the FPD response curve would be a function of both altitude and concentration. The CAPIN/FPD system has been field tested at other volcanos and at altitudes from sea level to 8 km (M.

Hart and J. Moyers, unpublished data). The response range of the instrument is approximately 2 ppbv to 3 ppmv, with a typical response time (80% full scale) of about 5 s.

The concentrations of sulfur gases were measured at Poás (February 17) and Colima (February 20) during coaxial penetrations of the plume. Table 4 is a summary of measurements of total sulfur concentration made during coaxial traverses through the Colima plume on February 20. The table shows the time and duration of in-plume measurement and the maximum and the average concentration of sulfur for the traverse. The large variation in the concentration of sulfur gas measured partly reflects the difficulty in keeping the aircraft in the densest portion of the plume during the traverse. The average concentrations of total sulfur most commonly ranged from 10 to 250 ppbv, but values as high as 1800 ppbv were recorded. The results from the direct measurements are in good agreement with the values calculated from the COSPEC/lidar data.

Particles: Size, Shape, and Composition

Particles in the plumes were sampled by using a quartz crystal cascade microbalance (QCM), a multistage cascade impactor that classifies particles into 10 size intervals by inertial impaction. A piezoelectric crystal microbalance senses the mass of particles on impact, thus providing the weight of each size interval as sampling proceeds. The samples are later analyzed by scanning electron microscope and energy dispersive X ray techniques with an electron microprobe to determine the morphology and elemental composition of the particles. This technique has been used to study particles from eruption clouds and plumes from volcanos in Guatemala [Rose *et al.*, 1980a], Mount St. Helens [Chuan *et al.*, 1981; Rose *et al.*, 1982], and Soufriere, St. Vincent [Woods and Chuan, 1982].

Samples for the QCM were collected during traverses that

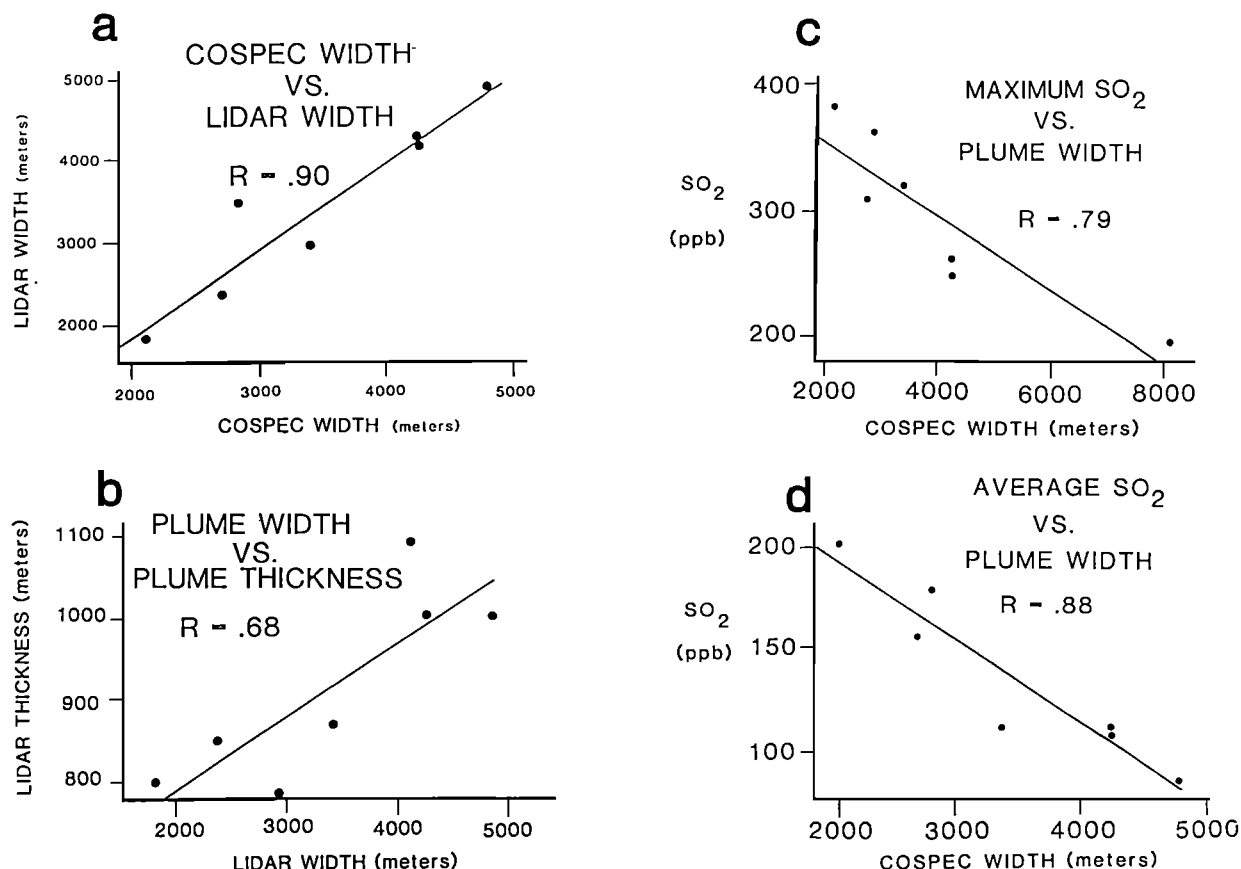


Fig. 4. (a) Plot comparing plume widths from COSPEC and lidar measurements, Colima, February 20, 1982. (b) Comparison of plume width and plume thickness as detected by lidar. Plume width and thickness increase simultaneously. (c, d) Plots of COSPEC plume width versus maximum and average SO₂ concentration calculated from COSPEC and lidar data.

penetrated the plumes, and high-quality data were obtained during the flights on February 17 (Poás) and February 20 (Colima). Figure 5 shows typical mass distributions of particles for plumes from Poás and Colima. Nearly all particles are finer than 3 μm (aerodynamic diameter). The peaks in the distributions of particles, which in both plumes are unimodal, are less than 0.35 μm . Both the distribution of particle sizes and the small average particle size serve to distinguish the quiescent plumes from plumes produced by explosive eruptive activity. For example, eruption clouds sampled in Central America [Rose *et al.*, 1980a] and at Soufriere [Woods and Chuan, 1982] contained particles that were larger than those

in the quiescent plumes studied here. The eruption clouds also contained larger concentrations of particles and have bimodal or trimodal distributions of particle sizes. These differences are most likely due to different eruptive mechanisms that include the fragmentation of molten rock and suspended crystals during explosive eruptions.

Two types of solid particles were commonly found in the quiescent plumes (Figure 6). These include silicate particles with irregular or angular shapes, which are probably glass shards and mineral fragments and, less commonly, fragments of Ca, K, and Na sulfate minerals. A thin film coated the silicate and sulfate particles collected from Poás and Colima, and energy dispersive analysis of material on the impactor stages indicates that sulfur is the dominant element of the film. The composition and morphology suggest that the film was probably derived from droplets of sulfuric acid. Much of the particle mass in the quiescent plumes is water, probably of meteoric origin [Rose *et al.*, 1980b], that condensed to produce a dilute liquid aerosol suspension. Solution of SO₂ into these droplets is inferred to produce the dilute sulfuric acid aerosol. Coalescence of these droplets produces a continuous coating over the solid particles. Cadle *et al.* [1969] examined particles from the quiescent plume of Arenal and determined that the plume was made up largely of droplets of dilute sulfuric acid. Earlier studies have also documented the abundance of sulfuric acid droplets in volcanic plumes [Cadle *et al.*, 1969; Rose *et al.*, 1980a; Woods and Chuan, 1982]. The sizes of

TABLE 3. Colima, Mexico: COSPEC-Lidar Measurements February 20, 1982

Time of Profile, s	SO ₂ COSPEC, ppm/m	Thickness Lidar, m	SO ₂ Concentration, ppb
0:47	5.1	186	27
0:44	120	770	156
0:41	248	780	317
0:38	170.1	780	217
0:35	55.3	680	78
0:32	53.3	680	78
0:29	29.7	580	51
0:26	20.5	400	51
0:23	6.15	283	22

TABLE 4. Summary of Measurements of Total Sulfur Gas During Coaxial Penetrations of the Plume at Colima, Mexico

Traverse Number	Time, hours:min	Maximum Concentration, ppbv	Average Concentration, ppbv
C2	18:21-28	251	66
C3	:30-34	301	68
C4	:35-39	301	38
C5	:41-44	234	96
C6	:46-49	293	91
C7	:51-54	171	54
C8	:55-58	800	74
C9	19:25-26	171	29
C10	:30-31	730	100
C11	:34-35	443	51
C12	:37-40	736	80
C13	:42-44	384	71
C14	:46-49	593	59
C15	:51-54	309	58
C16	:57-58	443	80
C17	20:00-03	1030	135
C18	:05-07	1100	209
C19	:09-11	1300	260
C20	:13-15	1887	70
C21	:17-19	836	235

such droplets in plumes generally ranges from 0.1 to 1.0 μm , which is the range of the particle sizes in the Poás and Colima plumes (Figure 5).

The total concentrations of small particles measured by the QCM were 4.7 $\mu\text{g}/\text{m}^3$ for Poás and 18.8 $\mu\text{g}/\text{m}^3$ for Colima. These particle concentrations are much lower than values (ranging from less than 50 to more than 700 $\mu\text{g}/\text{m}^3$) measured for eruption clouds that contain abundant silicate particles [Rose *et al.*, 1980a].

CONCLUSIONS AND DISCUSSION

Quiescent plumes are common features of many active volcanoes that erupt nonexplosively or that may not be in actual eruption. While quiescent plumes introduce the majority of volcanic sulfur and other volcanically derived volatiles present in the atmosphere [Berresheim and Jaeschke, 1983; Stoiber *et al.*, 1983], most studies of volcanic emissions have focused on the effects of the larger explosive eruptions, which occur much less frequently—Mount St. Helens (see *Science*, 211, 815–838, 1981), Soufriere (see *Science*, 216, 1105–1126, 1982), El Chichon (see *Geophysical Research Letters*, 10, 989–1060, 1983)—and which may inject material into the upper tropo-

sphere and stratosphere. The purpose of this study has been to examine the chemical and physical nature of quiescent volcanic plumes that remain in the troposphere. The main conclusions of this study are:

1. The quiescent plumes from Poás, Arenal, and Colima remained in the lower troposphere at altitudes of less than 4 km and were detectable up to at least 20 km downwind from their sources, the maximum distance at which measurements were made. The plumes were thickest at their centers and tapered at their edges, similar to plumes mapped at Mount Baker [Radke *et al.*, 1976] and Mount St. Helens [Casadevall *et al.*, 1981; Harris *et al.*, 1981] Washington, and at Mt. Etna (J. Carbonnelle, written communication, 1982) Italy.

2. The principal sulfur gas in the quiescent plumes studied here was SO₂. The good agreement between the calculated and direct measurements of SO₂ concentrations and the coincident shapes and widths of the lidar and COSPEC traces suggest that the plumes are well mixed by the time they are measured at distances of 1–20 km from the vent. This agreement also suggests that, at least up to 20 km from the volcano, most of the sulfur gas remains as SO₂ and that only a minor amount dissolves in the aerosol or is lost through conversion to sulfate.

3. The majority of particles in the plumes from Poás and Colima were smaller than 3 μm in diameter, and the peak in the unimodal distribution of particle sizes was less than 0.35 μm . Solid particles were rare and consisted mostly of fragments of rock-forming silicate minerals with minor sulfate mineral particles. The total concentration of small particles measured by the QCM was 0.0047 $\mu\text{g}/\text{m}^3$ and 0.018 mg/m^3 for Poás and Colima, respectively. The paucity of large particles and the ubiquitous sulfur-bearing film indicate that most of the particles in the plume are water droplets acidified by solution of SO₂.

4. The measured concentration of SO₂ in the plumes at Poás and Colima ranges from 10 to 250 ppbv, which corresponds to 0.026–0.65 mg/m^3 of SO₂, respectively. By comparing the concentration of SO₂ measured in the Poás plume (2–200 ppbv) with the concentration measured in the fumarolic gas (0.2–3 vol. %), we calculate that the plume has been diluted by a factor of about 100,000. This dilution factor is slightly greater than the range estimated for small eruption clouds [Rose *et al.*, 1980a]. Since some SO₂ that would otherwise escape in the Poás plume is probably dissolved in the crater lake, the dilution factor calculated for the Poás plume may be an overestimate.

5. Downwind dispersion caused the plumes to expand while being diluted. The maximum column densities of SO₂ measured at Colima by COSPEC decreased as the width of the plume increased (Figure 4c, d), while the SO₂ emission rates remained nearly constant. This suggests mass conservation of SO₂ in the plume, at least during the brief interval (less than 2 hours) between emission of the gas from fumaroles and measurement. This is consistent with the fact that conversion of SO₂ to SO₄²⁻ in the atmosphere is slow [Friend *et al.*, 1980] and depends on the availability of H₂O₂ and O₃ [Maahs, 1983]. COSPEC studies of the plume from the smelter at Mount Isa, Australia, indicate rates of SO₂ oxidation of between 0.15 and 0.25%/hr [Williams *et al.*, 1981].

6. Removal of SO₂ and particles from quiescent plumes is largely by sedimentation of larger particles to which SO₂ may be adsorbed [Rose, 1977], by rainout of water droplets that have absorbed SO₂ as well as particles and other acidic gases,

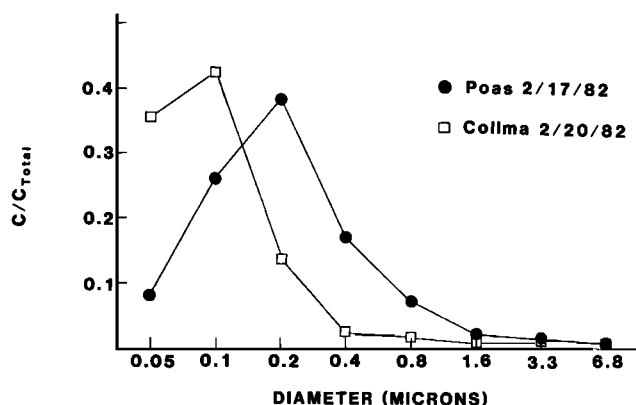


Fig. 5. Typical size distributions of particles for Poás and Colima.

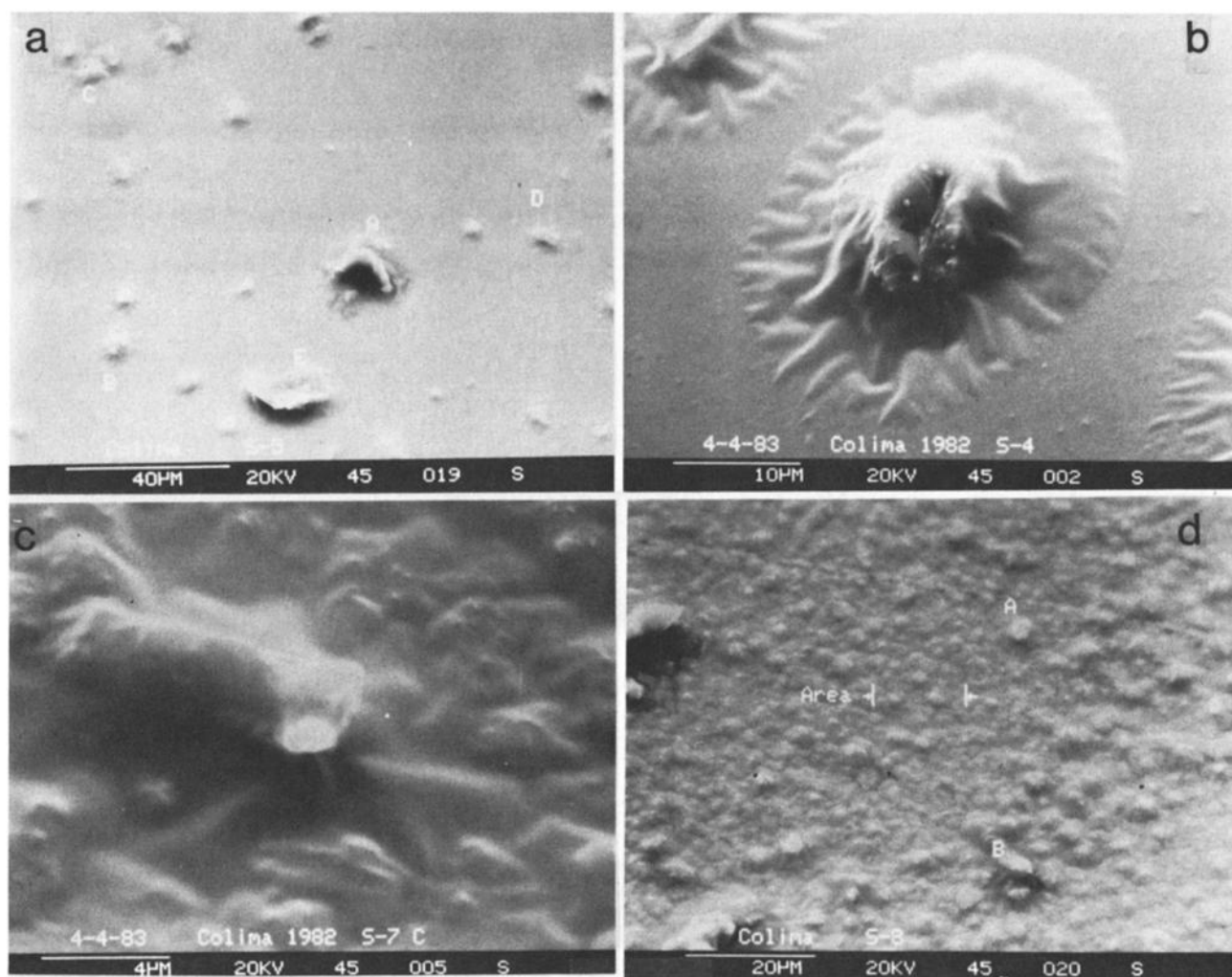


Fig. 6. Scanning electron micrographs of particles from the Colima plume. In general we infer three kinds of particles: (1) silicate rock and mineral fragments, usually with acid coatings, (2) solid sulfates, and (3) dilute sulfuric acid liquid. (a, b) Samples of larger particles from stages 4 and 5 of the QCM. In (a), particles A and C are Ca and S rich, as revealed by energy dispersive analysis. We infer them to be CaSO_4 (hydrated?). Particle B is probably a pyroxene fragment with an acid coating. D is probably a plagioclase. (b) Silicate rock fragment heavily coated with a sulfur-rich liquid, which has evaporated. (c) The more crowded terrain of stage 7 and a particle rich in K, S, and Na. We infer it to be aphthalite ($\text{K}_3\text{Na}(\text{SO}_4)_2$), which is a common incrustation mineral at fumaroles. (d) From stage 8, small particles covered in a sulfur-rich liquid. Particles A and B are silicates, but the spectral signal of the marked "area" shows only sulfur in the energy dispersive pattern. We infer it to be dilute sulfuric acid.

and by dry deposition onto vegetation and soil. The lifetime of these quiescent volcanic plumes is short, probably hours to days, compared to the longer residence times (months to years) of eruption plumes injected into the stratosphere. To have an appreciable affect on atmospheric chemistry, quiescent plumes must either overwhelm the tropospheric scrubbing mechanisms or they must eventually enter the stratosphere, where removal mechanisms such as rainout are less efficient.

Quiescent Plumes at Volcanos

Unlike stationary anthropogenic sources of SO₂, such as coal-fired power plants and smelters that steadily emit SO₂ over decades, the production of SO₂ from a volcano is often short-lived, usually months to years, and varies with eruptive activity. The emission rates of SO₂ in volcanic plumes have been measured regularly at several volcanos, such as Mount St. Helens [Casadevall et al., 1981, 1983], Kilauea, Etna [Ma-

linconico, 1979; J. Carbonnell, written communication, 1982], and Galunggung and Merapi, Indonesia (M. Badrudin, personal communication, 1984). The variations in the emission rates with eruptive activity are used to provide information for monitoring volcanic activity. The SO₂ and CO₂ emissions rates measured in the quiescent plume at Mount St. Helens [Casadevall et al., 1983] declined rapidly after explosive eruptions of 1980 and continued to decline more slowly in 1981–1983. In a generalized way the declining gas emissions mimicked the explosiveness of eruptive activity, which also declined. Available data on SO₂ emission rates and timing of eruptions at the other volcanos suggest that gas emissions that are generally in the range of 100–2000 t/d show patterns broadly sympathetic to volcanic activity.

Mass balance calculations made from sulfur gas emission data indicate that more magma is outgassed with respect to sulfur than is actually erupted [Casadevall et al., 1983]. Additional data are needed to further explore the analogies, but

we suggest that the plumes from Poás, Arenal, and Colima depict typical quiescent plumes and are the result of degassing following shallow (1–10 km depth) emplacement of calc-alkalic magma bodies that are generally 0.1–3 km³ in volume.

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