

Geochemical surveillance of magmatic volatiles at Popocatépetl volcano, Mexico

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ABSTRACT

Surveillance of Popocatépetl volcanic plume geochemistry and SO₂ flux began in early 1994 after fumarolic and seismic activity increased significantly during 1993. Volatile traps placed around the summit were collected at near-monthly intervals until the volcano erupted on December 21, 1994. Additional trap samples were obtained in early 1996 before the volcano erupted again, emplacing a small dacite dome in the summit crater. Abundances of volatile constituents (ppm/day of Cl, S_{total}, F, CO₂, Hg, and As) varied, but most constituents were relatively high in early and late 1994. However, ratios of these constituents to Cl were highest in mid-1994. δ³⁴S-S_{total} in trap solutions ranged from 1.5‰ to 6.4‰; lowest values generally occurred during late 1994. δ¹³C-CO₂ of trap solutions were greatly contaminated with atmo-

spheric CO₂ and affected by absorption kinetics. When trap data are combined with SO₂ flux measurements made through November 1996, Popocatépetl released about 3.9 Mt SO₂, 16 Mt CO₂, 0.75 Mt HCl, 0.075 Mt HF, 260 t As, 2.6 t Hg, and roughly 200 Mt H₂O. Near-vent gas concentrations in the volcanic plume measured by correlation spectrometer (COSPEC) and Fourier transform infrared (FTIR) commonly exceed human recommended exposure limits and may constitute a potential health hazard. Volatile geochemistry combined with petrologic observations and melt-inclusion studies show that mafic magma injection into a pre-existing silicic chamber has accompanied renewed volcanism at Popocatépetl. Minor assimilation of Cretaceous wall rocks probably occurred in mid-1994.

INTRODUCTION

Popocatépetl (5452 m) is an andesitic strato-volcano located in the eastern half of the Trans-Mexican volcanic belt 70 km southeast of downtown Mexico City (Fig. 1). Popocatépetl had several pre-Hispanic eruptions that had dramatic cultural impact because of their magnitude and

widespread distribution of pyroclastic deposits. The latest cycle of major pyroclastic activity occurred about 1150 B.P. and devastated major urban centers that once existed east of the volcano (Siebe et al., 1996b, 1997; De la Cruz and Siebe, 1997). The most recent historic eruption (A.D. 1919 to 1927) built a dacite dome in the crater. From 1927 through 1986, Popocatépetl was relatively quiet. Fumaroles in the summit crater had temperatures <100 °C and a small, cold crater lake had a pH of 4 to 5. Increased fumarolic activity was noticeable by 1993. In addition, the crater lake became milky green and summit ice around the crater became encrusted with sulfur (Delgado et al., 1997). By February 1994, some crater fumaroles had reached temperatures of 400 °C and the lake reached temperatures >60 °C with a pH of about 1.5 (measured at 25 °C).

Increased seismicity and fumarolic activity during 1993–1994 instigated several surveillance activities (Comité Científico Asesor, 1996), including monitoring of volcanic plume discharges by correlation spectrometer (COSPEC) and sampling of fumarolic emissions using volatile traps placed around the upper crater rim. The traps contained a solution of 4N KOH that absorbed acids and volatile metals from gases and aerosols

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Data Repository item 9832 contains additional material related to this article.

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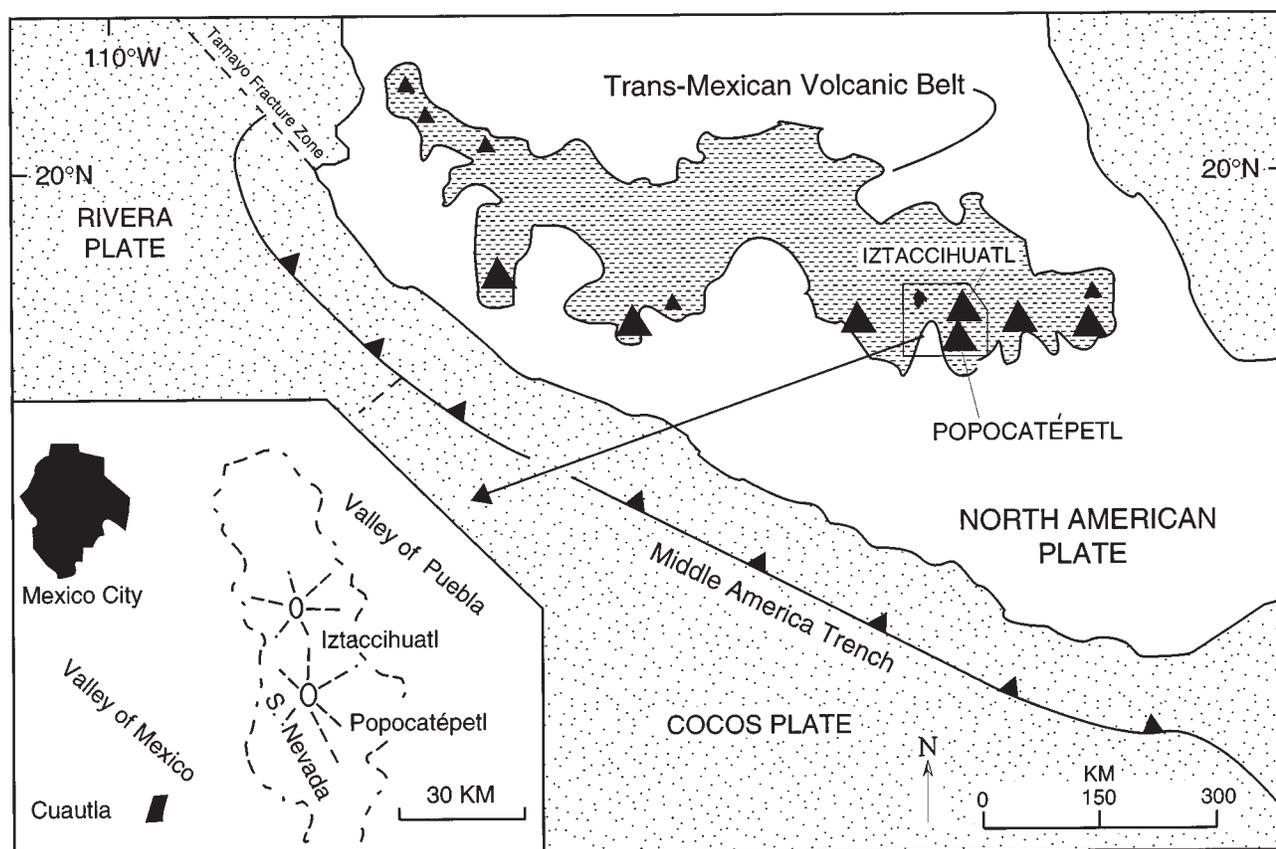


Figure 1. Regional map of the Trans-Mexican volcanic belt and a detailed map (inset) of the area near Popocatépetl (modified from Robin and Boudal, 1987).

in the volcanic plume. The traps were sampled at near-monthly intervals beginning in February 1994 until the phreatic eruption of December 21, 1994. SO_2 flux measured by COSPEC averaged about 2000 t/day during 1994 but rose to values of ≤ 8000 t/day during much of 1995.

A few volatile trap solutions were collected in early 1996, during a lull in volcanic activity. In March 1996 a small dacite lava dome was emplaced in the crater and periodic explosions were reported thereafter. By January 1997, SO_2 flux had risen erratically to values as high as 50 000 t/day and another flow lobe of dacite was emplaced in the crater (H. Delgado, 1997, unpublished data). Popocatépetl is currently one of the world's largest natural emitters of SO_2 (and probably most other volcanic gases) to the atmosphere.

The main objectives of our project were to determine if temporal changes occur in volatile geochemistry and to evaluate whether these changes were related to specific magmatic processes. A secondary goal was to combine geochemical results with SO_2 fluxes and chemical ratios determined by remote sensing instruments to estimate the fluxes of several

other volatile components degassing from Popocatépetl during 1994 to early 1997.

GEOLOGIC SETTING AT POPOCATÉPETL

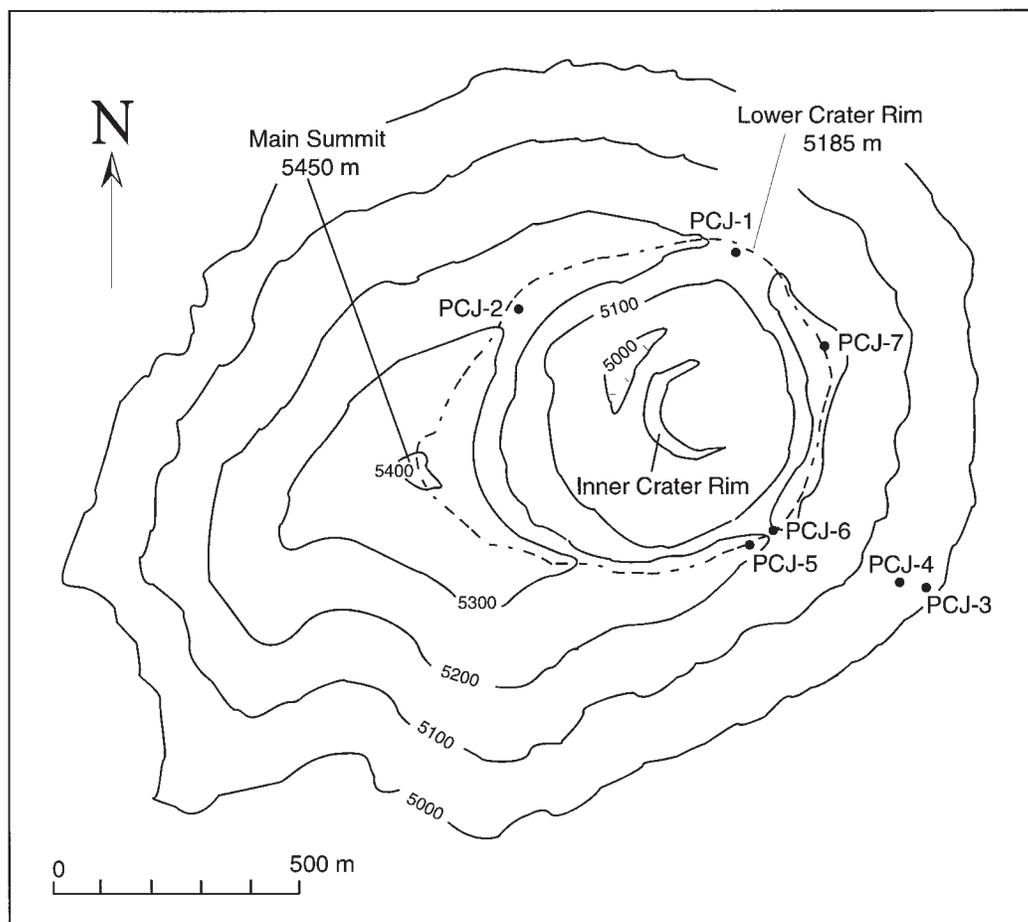
Popocatépetl ("smoking mountain") is in the eastern half of the Trans-Mexican volcanic belt, which extends approximately east-west from the Gulf of Mexico to the Pacific Coast (Fig. 1). The belt averages 900 km in length and 100 km in width. The Middle America Trench lies south of the Trans-Mexican volcanic belt, varying in distance from 350–450 km in the east to 200 km in the west (Robin, 1982).

Popocatépetl is located in the southern portion of the Sierra Nevada, which borders the southeast margin of the Valley of Mexico (Fig. 1). Iztaccihuatl (5286 m), another major volcano in the Sierra Nevada, is located 15 km north of Popocatépetl. The Valley of Mexico is an enclosed basin located in the central portion of the Trans-Mexican volcanic belt and is about 100 km long by 30–60 km wide (Mooser et al., 1974). Several articles by Nixon and coworkers (Nixon et al., 1987; Nixon, 1988a, 1988b, 1989) described the geology of the

Valley of Mexico and Iztaccihuatl and proposed that eruptive activity for all major volcanoes in this region began 1.7 Ma. On the basis of K-Ar dating of lavas, eruptive activity at Iztaccihuatl began before 0.9 Ma and continued until ca. 10 ka. Rock types found at Iztaccihuatl are predominantly calc-alkaline andesite and dacite that display mineralogical and chemical evidence for mixing of a dacitic magma with a primitive, olivine-bearing, mafic end member.

Work on the evolution, petrology, and dating of Popocatépetl was initiated mainly by C. Robin, C. Boudal, and J. Negendank in the 1970s and 1980s. The volcano consists primarily of two-pyroxene andesite with subordinate dacite and flanking basalt and basaltic andesite. The eruptive history of Popocatépetl has been divided into two periods; the birth (probably < 1 Ma, Delgado et al., 1988) and construction of an ancient stratovolcano, Nexpayantla, and the most recent volcanism, which created the modern volcano. Nexpayantla was destroyed by gravitational collapse, which occurred between 24 and 22 ka as evidenced by the presence of a large debris avalanche deposit toward the south (Siebe et al., 1996a, 1997). The primitive cone

Figure 2. Map of Popocatépetl summit showing positions of volatile traps around the lower crater rim and on the southeast side of the crater.



is exposed on the northwest and west flanks of the volcano and is marked by a change in slope (Negendank, 1972; Boudal, 1985; Robin and Boudal, 1987).

The present cone consists mostly of interlayered lavas and pyroclastic deposits of andesitic to dacitic composition. During the past 22 k.y, activity was characterized by at least seven large Plinian eruptions occurring in time intervals of 1000 to 3000 yr, as determined by ^{14}C dating of pyroclastic deposits on the modern cone (Cantagrel et al., 1984; Boudal and Robin, 1988; Siebe et al., 1996b). The last three major eruptions occurred between 3195 to 2830 B.C., 800 to 215 B.C., and A.D. 675 to 1095 (Siebe et al., 1996b). The only well-documented historic activity took place between A.D. 1919 and 1927, during which a 215-m-high dome was emplaced inside the present crater (Waitz, 1921). Activity commencing in December 1994 has mainly consisted of pulsating emissions of ash (Delgado et al., 1995) and caused the temporary evacuation of 75 000 people when the first phreatic explosions occurred. Tephros and an intracrater dome appearing in March 1996 consist of hornblende dacite having 62–64 wt% SiO_2 (Stimac et al., 1997).

The Sierra Nevada is known to be intercalated with a Tertiary to Quaternary sedimentary and volcanic terrain (Chichinautzin Group of Mooser, 1957) and overlies Cretaceous to Tertiary carbonate and evaporite rocks. These deposits are not exposed in the Valley of Mexico, but Cretaceous strata are exposed as isolated outcrops related to horst and graben fault structures at distances more than 20 km south of Popocatépetl's summit. These deposits are surrounded by laharic-fluvial sequences and debris-avalanche deposits from Popocatépetl (Siebe et al., 1997).

VOLATILE TRAP STUDY

Active volcanoes that have been closely monitored during eruptive episodes usually show short-term variations in the chemical and isotopic composition of their emissions (Tedesco, 1995). The volatile trap ("alkaline" trap) method was devised by Noguchi and Kamiya (1963) to collect wind-dispersed volcanic vapors, and has been employed at several volcanoes (i.e., Williams et al., 1990; Italiano et al., 1991). When direct sampling is not feasible, traps are used to monitor fumarolic emissions over a sampling interval of

days to weeks, providing indirect observations of bulk concentrations, concentration ratios, and isotopic composition with time. Because sampling intervals can be as long as a month or more, volatile variations that occur during short time intervals are averaged.

Italiano et al. (1991) presented a generalized function showing that the concentration of any volatile species fixed in the trap solution is dependent on many factors: time, volatile flux from the fumarolic source, meteorological conditions, geometry of the trap container, surface area of the trap solution, and absorptivity efficiency of the trap solution. Volatile concentrations are also affected by exponential dilution of fumarole gas by air with increasing distance from source to trap (Le Guern and Faivre-Pierret, 1982). Furthermore, some gas components undergo reactions after fumarole discharge. For example, sulfur gases can react with oxygen in air, or can react in the large temperature gradient between fumarole discharge and ambient air to form new gas compounds and sublimates. Acidic gases are water soluble and can be partially "rained out" during periods of heavy precipitation before reaching the trap solution.



Figure 3. Photograph of Popocatépetl crater before 1993; vertical walls are approximately 250 m deep and the crater diameter is approximately 1 km. Due to the extreme danger related to direct sampling of fumaroles (located on the floor and walls of the crater), volatile traps were placed around the crater rim.

Collection and Analysis of Volatile Trap Samples

Seven volatile traps were placed around the crater of Popocatépetl during 1994; two just inside

the lower crater rim, three on the crater rim and two outside the crater (Fig. 2). Major high-temperature fumaroles are only found inside the summit crater and were considered too dangerous to sample directly (Fig. 3). Sampling of the gas plume ris-

ing from the crater was complicated by regional wind directions (Delgado et al., 1996), generally to the east in the dry season (November to April) and to the west in the rainy season (May to October). Samples were obtained from each trap at near monthly intervals where possible, but not all stations were active for each month of the study.

The volatile traps consist of a plastic beaker approximately 20 cm high by 15 cm wide containing 500 ml of 4N KOH (Fig. 4). The traps were placed beneath inverted, ventilated buckets, which allowed gases to contact the caustic solution, yet protected the solutions from major contamination by meteoric water precipitation and rock fragments. Wind-blown dust and sublimates could still enter the trap under certain conditions. The caustic solution absorbed reactive gases (CO_2 , SO_2 , H_2S , HCl , and HF) and volatile metals (e.g., As, Hg). However, nonacidic components such as H_2O , He, H_2 , O_2 , Ar, N_2 , CO, and CH_4 were not absorbed by the caustic solution. Some CO may have reacted with KOH to produce formaldehyde, but this constituent was not analyzed. The loss of these various gases is a disadvantage of volatile trap sampling compared to direct sampling in which all fumarolic species are captured (Fahlquist and Janik, 1992).

Details of chemical analysis methods and detection limits for species analyzed during this study were listed in Trujillo et al. (1987) and Werner et al. (1997). In particular, aliquots of sample solutions were treated with 30% hydrogen peroxide (H_2O_2) to convert all sulfide, elemental sulfur, and sulfite to sulfate. Aliquots were analyzed for Cl, F, and SO_4 (reported as total S) by ion chromatography, and for CO_3 by titration with standard HCl: detection limits for these constituents were 1, 1, 5, and 10 ppm, respectively. Separate aliquots were removed for analysis of As by the hydride generator-graphite furnace AA method and for Hg by the cold vapor AA technique. Detection limits were 1 ppb for As and 0.2 ppb for Hg. Additional aliquots of the trap solutions were prepared and analyzed for carbon and sulfur isotope compositions using methods described in Fahlquist and Janik (1992). Atmospheric blanks were set out away from the volcano at various localities to estimate background levels of the measured constituents. These samples showed negligible amounts of all constituents except CO_3 .

Chemical Behavior of Gases in Alkaline Solutions

The 4N KOH solution is a very efficient chemical "sponge" for acid gases, although solubilities and reaction kinetics of the major gases vary. Gaseous HCl, HF, and H_2S neutralize caustic solution to form chloride, fluoride, and sulfide ions. CO_2 also neutralizes caustic forming carbonate

ions, which make up as much as 90% of the dissolved species in many samples. The potassium salts of the above four anions are very soluble in alkaline conditions (≥ 340 g/l of cold solution depending on salt; CRC, 1994) and saturation with respect to these salts was never attained in our samples. SO_2 reacts initially with caustic to form sulfite, which is also soluble in alkaline solutions. With time, sulfite oxidizes irreversibly to sulfate. K_2SO_4 is the least soluble of the major components (120 g/l), but no solution was saturated with sulfate (even assuming that S_{total} was originally in the form of SO_4).

Of the 57 trap solutions, 5 absorbed sufficient vapors to neutralize the caustic gases, yet continued to absorb more acid gases (the most concentrated sample contained 2.55 mol of major anions in a 500 ml sample, assuming all S to be SO_4). The reacted KOH solutions do not represent equilibrium conditions and resulting data contain chemical uncertainties. However, the volatile trap method is currently the only way to assess multi-component variations in plume geochemistry when direct sampling of high-temperature fumaroles is too difficult or dangerous. With increased volcanic activity, the flux of volatile species may be so large (>1000 t/day) that the physical and chemical limitations described here are partially negated by relative volatile abundance. Because total absorbed concentrations of species in the trap solutions vary tremendously, we have used the ratios of species to assess relative uncertainties (discussed below).

GEOCHEMICAL VARIATIONS IN FUMAROLIC GASES

Chemical and isotopic analyses of the volatile trap solutions are listed in Table DR1¹ according to station number, collection date, and number of days of use. Also listed are ratios of Cl, CO_3 , F, As, and Hg with respect to SO_2 to assist with COSPEC correlations. The time intervals vary somewhat among sampling sites because of difficulties with installing and changing the traps. The analyzed concentrations are divided by the number of days that the trap was in place to obtain average daily concentrations. This removes short-term chemical variations and permits observation of relative changes in normalized concentration on a near-monthly basis: even so, complex trends are revealed (Fig. 5). Chemical abundances vary with location around the crater rim for any one collection period, probably due to complicated wind patterns, changing fu-

¹GSA Data Repository item 9832, tables of chemical and isotopic analyses and ratios to assist with COSPEC correlations, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301. E-mail: editing@geosociety.org.



Figure 4. Photograph showing collection of a volatile trap sample on the crater rim of Popocatépetl.

marolic discharge rates and bulk compositions, and other variables. In some cases, concentrations behave erratically among stations, suggesting that winds have blown dust and sublimates with variable chemical composition into some traps, but not others (Werner et al., 1997).

In spite of the noisy data, general compositional trends demonstrate actual volatile changes throughout the sampling period. Average daily concentrations of S, F, and Hg (Fig. 5, A, B, and C) are highest for one or more stations in the June and July collecting periods. The plot of As/day versus time (Fig. 5F) shows higher concentrations in the earlier months of the year and decreasing values toward mid to late 1994. Cl/day also tends to be highest in the earlier and later months, although a small peak is observed in the July collection (Fig. 5D). The plot of CO_3 /day versus time (Fig. 5E) shows variability for all stations, which probably reflects contamination with atmospheric CO_2 as well as absorption of fumarolic CO_2 . The lowest CO_3 /day values are obtained from the August to October collections. All plots except As/day and F/day show an increase in species abundance during the last sampling period, probably marking the onset of eruptive activity that began in December 1994.

Ratios of S/Cl and F/Cl have been used previously to forecast tentative eruptive activity (Italiano, 1991). Cl ratio diagrams shown in Figure 6 use the average chemical ratio of all stations for a certain collection period. The highest values for S/Cl and F/Cl occurred in June, whereas As/Cl,

Hg/Cl, and CO_3 /Cl show respective highs in July. These highs bracket a relative increase in SO_2 flux measured on July 2 and correspond with generally lower Cl concentration during these months (Fig. 5). The first sampling period in February also shows increased values of S/Cl, F/Cl, and As/Cl. After July, the ratios of all species stay at relatively low values through the rest of 1994. Only two stations were reoccupied in early 1996. All values during 1996 are relatively low except for an anomalous As/Cl value in January 1996 (Fig. 6).

We can assess the statistical uncertainty of the volatile trap data by taking the standard deviation (1σ) of the average ratio for each collection period and calculating a percent error. The range of values, which is huge, is as follows: S/Cl (2%–112%); F/Cl (0.1%–119%); As/Cl (3%–210%); Hg/Cl (6%–180%). In general, collection periods with fewer stations have larger uncertainties, although there are exceptions. The average As/Cl value measured for two samples in January 1996 has an uncertainty of only 3%.

Despite the chemical uncertainties, irregular sampling intervals, and variations in meteorological conditions, the data clearly indicate major geochemical trends in volatile compositions.

Sulfur Isotope Geochemistry

Extremes in $\delta^{34}\text{S}$ (Fig. 7A) occurred in July samples from the northwest (overall maximum 6.5‰) and the southeast (minimum 2.3‰), fol-

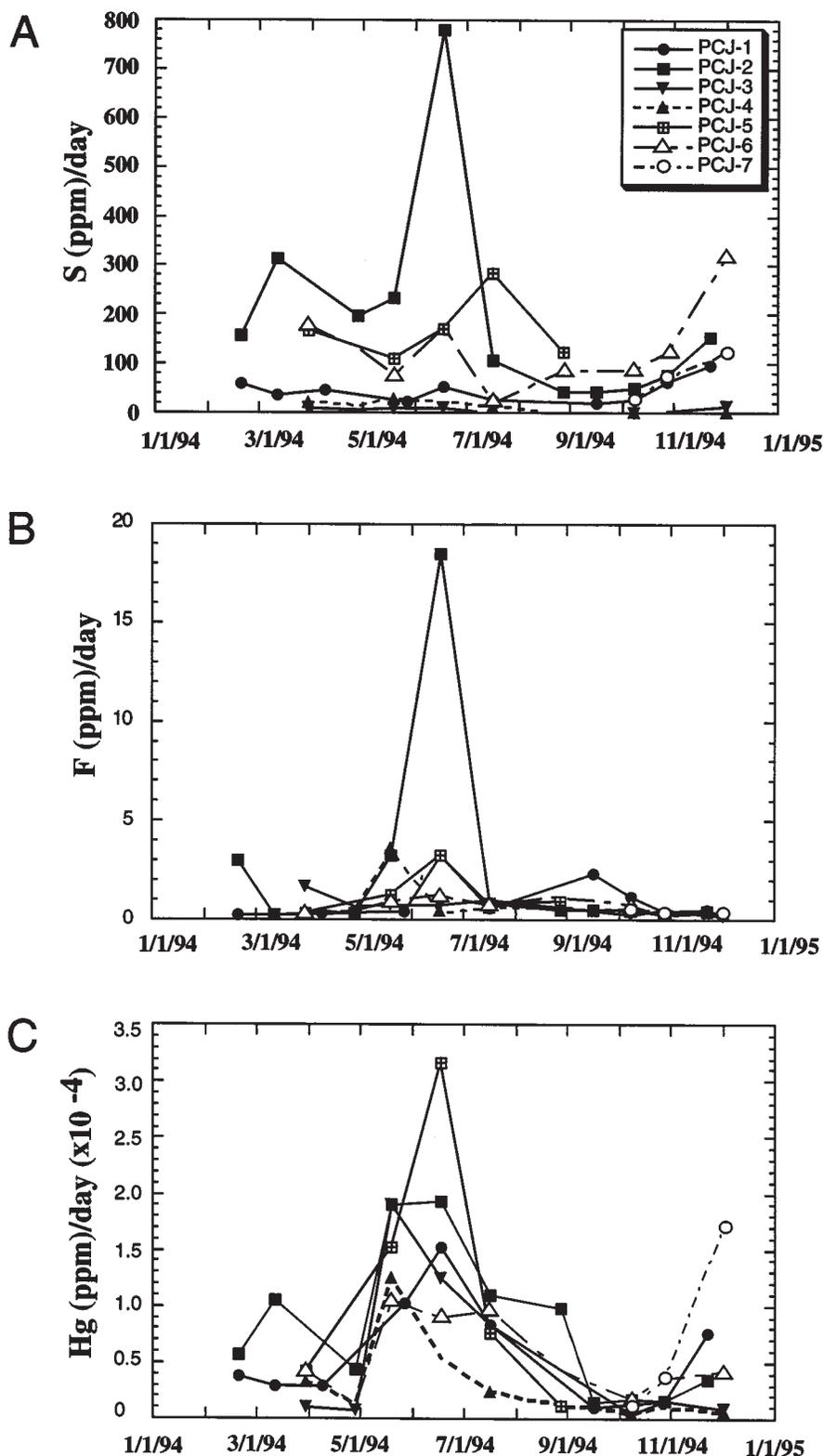


Figure 5. (A–F) Concentrations (ppm) per day of constituents measured from the seven volatile-trap stations located around the crater of Popocatepetl. Note the three trends in the data: The first trend shows broad highs in Cl, CO₂, and As during early 1994. The second shows peaks in S, F, Hg, and Cl during mid-1994. The third shows increases in all components except As and F before the eruption in December 1994.

lowed by a steady increase to October in $\delta^{34}\text{S}$ from the southeast (to 5.4‰). These data are coupled with increased seismicity and high SO₂ flux (3100 t/day) reported in July. The higher $\delta^{34}\text{S}$ values could indicate a small contribution of heavy sulfur derived from nonmantle sources (Fig. 8A). The $\delta^{34}\text{S}$ analyses of SO₄ dissolved in the crater lake water and gypsum from a regional evaporite deposit yielded values of 18.6‰ and 16.4‰, respectively. The heavy isotope value for sulfur in the lake is consistent with a fractionation of about +20‰ between SO₂ and dissolved SO₄ at temperatures of about 100 °C (Sakai, 1968). The isotope value obtained for the gypsum is normal for Cretaceous evaporites (Ohmoto and Rye, 1979).

Between October and early December, all locations had decreasing $\delta^{34}\text{S}$ values (to an overall minimum of 1.5‰) along with increasing S_{total}, CO₂, F, and Cl concentrations. $\delta^{34}\text{S}$ analysis of native sulfur deposited near the crater is 1.3‰. These values are close to the values for mantle-derived sulfur (Fig. 8A). The combined trends probably reflect gases released from magma prior to the eruption, and a more primordial origin of the sulfur gases released after October 1994 when $\delta^{34}\text{S}$ approached the value of about 1‰.

Experiments on kinetic sulfur isotope fractionation for SO₂ in air indicate that about a –1‰ shift can be expected as gas leaves the volcanic vents and absorbs into the trap solutions (P. M. Nuccio, unpublished data). Thus, our sulfur isotope results could be 1‰ more depleted than actual values. If so, the corrected values would imply that there is a slightly larger contribution of sulfur from nonmantle sources than indicated. Our average value for 41 sulfur isotope measurements of Popocatepetl gases is +3.35‰ ± 0.92‰, within the range for volcanic SO₂ and slightly heavier than sulfur of mantle origin. In the only other published study of sulfur isotopes from volatile trap samples, Williams et al. (1990) obtained an average value of +1.9‰ ± 1.2‰ (*n* = 5) for Nevado del Ruiz volcano, Colombia.

Carbon Isotope Geochemistry

The $\delta^{13}\text{C}$ values ranged from –25.8‰ to –9.3‰ (Fig. 7B), and generally decreased with increasing CO₂ contents, opposite of the expected trend for higher contributions of volcanic CO₂. Two samples of Popocatepetl fumarole gases collected from the crater rim in November 1993 had an average $\delta^{13}\text{C}$ -CO₂ of –6.54‰ ± 0.01‰ (T. Lorenson and W. C. Evans, unpublished data). Mantle $\delta^{13}\text{C}$ ranges from –8‰ to –3‰; the mean value is about –6‰ (Rollinson, 1993; Fig. 8B). As the KOH solutions trapped both atmospheric and volcanic CO₂, reaction kinetics apparently favored the light isotope

(Craig, 1953; Rollinson, 1993). CO_2 evolved from a blank placed on the flank of Popocatepetl outside the influence of fumarolic activity yielded $\delta^{13}\text{C}$ of -24.4‰ , much lower than the value expected for atmospheric CO_2 (-7‰ ; Craig, 1953; Ohmoto and Rye, 1979). Although the air around Popocatepetl is polluted with a 5% relative addition of anthropogenic CO_2 from urban combustion of fossil fuels (Gerlach et al., 1997), it is unlikely that the value obtained from the blank represents the $\delta^{13}\text{C}$ of local atmospheric CO_2 . Kinetic fractionation by preferential absorption of isotopically lighter CO_2 is the dominant process in collecting CO_2 using alkaline solutions (see Craig, 1953, p. 71–72). A set of KOH blank solutions placed on the lab bench at the U.S. Geological Survey in Menlo Park during analyses of the trap samples yielded an average $\delta^{13}\text{C}$ value of -16‰ .

In spite of these kinetic effects, the heaviest carbon isotope values from the trap samples correspond to the October maximum in $\delta^{34}\text{S}$ for the southeast traps. This peak in $\delta^{34}\text{S}$ is consistent with an increase in magmatic carbon, but cannot rule out a small contribution of carbon from regional limestone deposits being assimilated into the magma chamber. Two locations show a trend toward higher $\delta^{13}\text{C}$ values (a more mantle origin) in the two months prior to the eruption on December 1994, coincident with the observed decrease in $\delta^{34}\text{S}$ from October through December. We conclude that $\delta^{34}\text{S}$ is much more useful and reliable than $\delta^{13}\text{C}$ as an indicator of increased volcanic activity when monitoring fumarolic emissions with volatile traps.

IMPLICATIONS FOR ERUPTION FORECASTING

The volatile trap method was not effective for eruption forecasting during 1994 and 1996 due to logistical and analytical limitations. Popocatepetl is 5452 m high; thus, servicing the traps required periodic visits by scientists trained for high-altitude mountaineering conditions. Once the volcano erupted in December 1994, servicing these traps on a regular basis was considered to be too dangerous. The samples were analyzed in the United States, and the lag-time between sample collection and data acquisition was several weeks at best. However, the data (once acquired) showed significant changes in volatile geochemistry that correlated with increased SO_2 emissions (discussed in the following) and provided much insight on magmatic processes. In hindsight, it appears that volcano monitoring with volatile traps might be very useful for situations where direct fumarole sampling is impossible yet the summit area is accessible. Volatile traps should be considered an important part of the

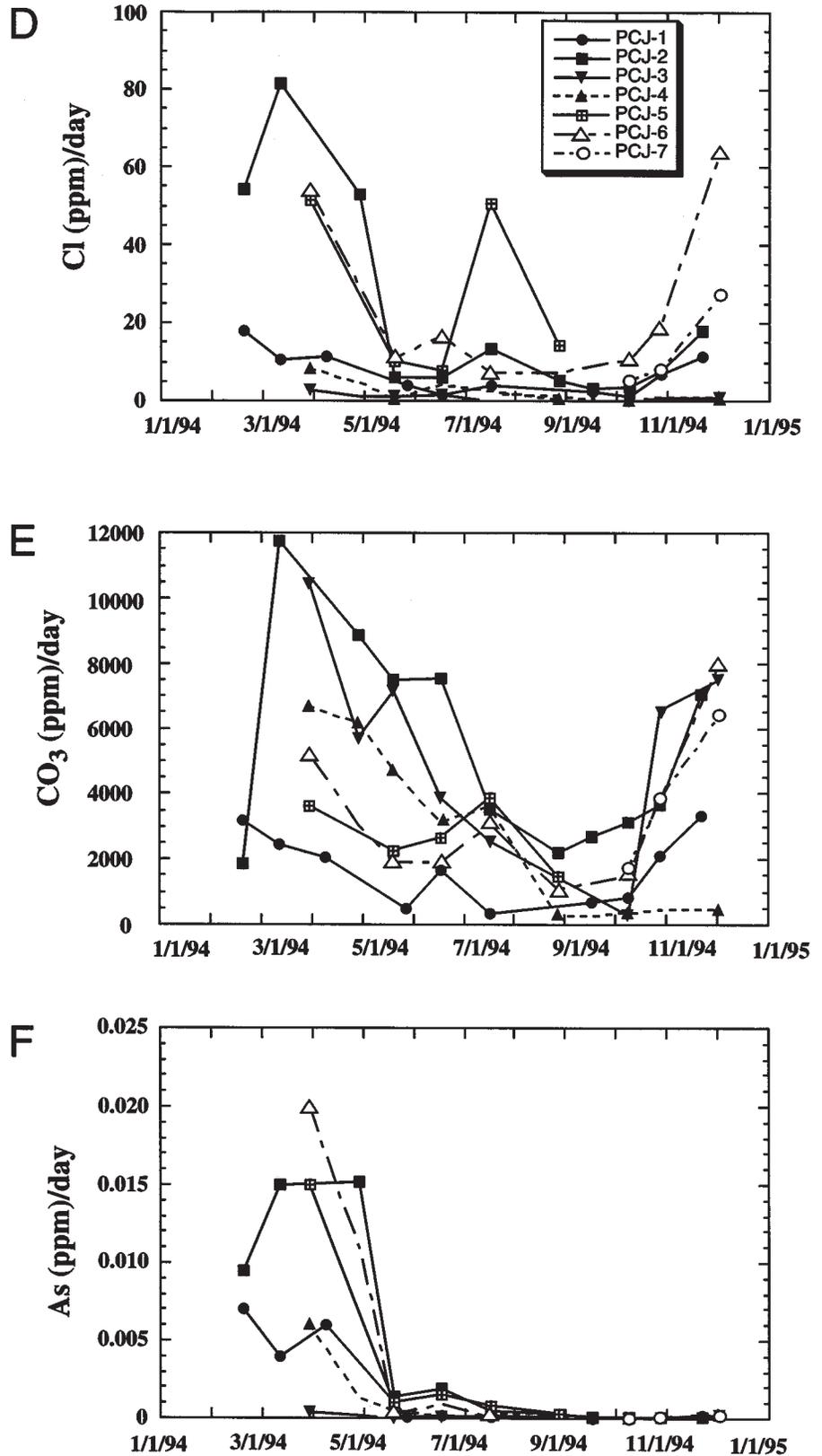


Figure 5. (Continued)

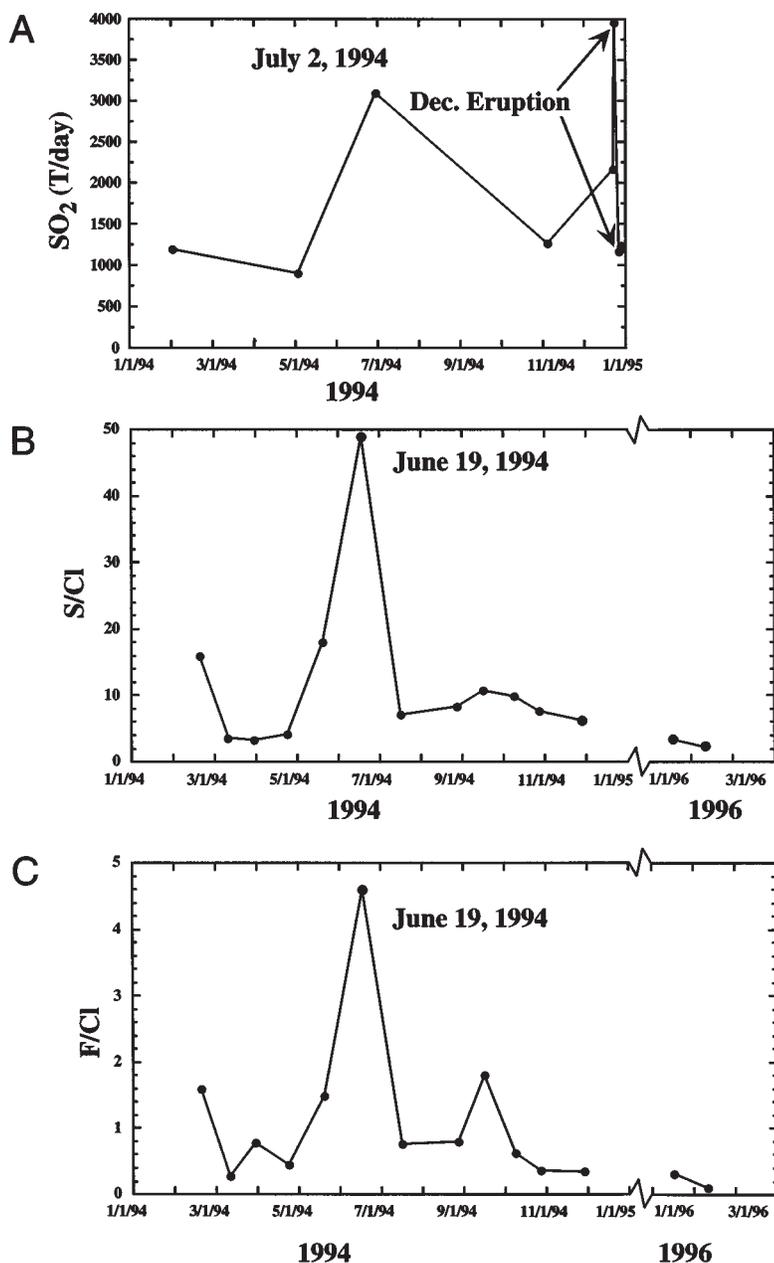


Figure 6. (A) SO₂ flux measured by COSPEC during 1994; (B–F) Cl ratio diagrams use average values for a particular collection period. Highs in S/Cl and F/Cl occur before the apparent high in SO₂ flux measured on July 2. As/Cl, Hg/Cl, and CO₃/Cl show respective highs after July 2. Although the CO₃ values are highly suspect due to air contamination, trends in CO₃ are nonetheless similar to other volatile components.

monitoring program. Plastic buckets, glassware, and KOH are relatively inexpensive and easily purchased. Portable equipment (titrators and specific ion electrodes) can be readily acquired for rapid analysis of CO₃, Cl, F, and SO₄ to ±5% accuracy. This equipment can be set up in a small space at a volcano monitoring headquarters. In-

stallation of a portable anemometer with telemetering capability could help with interpretation of wind patterns that affect trap measurements, if such a device could be protected from explosions and other hazards. Timely results could contribute significantly to the integrated data sets used in eruption forecasting.

FLUX OF VOLATILE SPECIES

COSPEC SO₂ measurements listed in Table 1 were obtained using a Barringer (model V) instrument. The COSPEC passively measures SO₂ concentration using ambient ultraviolet (UV) light. SO₂ absorbs UV light at 290–320 nm. By comparing the plume signal to sunlight, and using an internal standard, SO₂ concentrations in parts per million-meter (ppm-m) are obtained. Flux (or mass discharge rate) is calculated by multiplying measured plume cross-section and estimated plume velocity by SO₂ concentration (see Rose et al. [1986] and Kyle et al. [1994] for descriptions and interpretation of data). The determination of plume concentration is the most sensitive measurement since the COSPEC can observe SO₂ concentrations as low as 2 ppm-m. Larger errors are inherent to measurements of plume cross-section and windspeed. The windspeed was measured using global positioning system (GPS) techniques on a plane or obtained from a local airport. Total relative errors are usually between 10% to 30% but can be larger depending on conditions.

SO₂ measurements were made from an airplane flying beneath and perpendicular to the plume and from a vehicle driving beneath and perpendicular to the plume, where possible (Galindo et al., 1996). These measurements yielded an average SO₂ flux for 1994 of about 2000 t/day. Since that time, values reached 10 000 to 15 000 t/day through much of 1995–1996 and climbed to 60 000 t/day during at least one day in February 1997, temporarily making Popocatepetl the largest subaerial natural producer of SO₂ in the world (Delgado et al., 1995; Delgado and Cardenas, 1997).

Atmospheric Carbon Dioxide Contamination

To calculate expected CO₂ flux ranges while the traps were emplaced on the volcano and to evaluate the amount of excess atmospheric CO₂ absorbed by the traps (Table 2), we used CO₂/SO₂ ratios of 2 to 6, which were determined for the volcanic plume gases by combinations of remote sensing methods (Gerlach et al., 1997; S. Williams, unpublished data, 1996). Comparison of these calculated values to the values in Table 1 indicates that the traps usually contain 10% to 60%, and possibly as much as 99% atmospheric CO₂. Trap samples with the highest proportions of atmospheric CO₂ are generally those from sampling points most exposed to summit winds. Surface agitation of the trap solutions by winds probably promotes mixing and additional CO₂ absorption.

Another way to qualitatively evaluate atmospheric contamination is to compare the amounts

of CO_3 analyzed in the blank solutions to the amounts determined from volcano samples (Table DR1; see footnote 1). Blank solutions usually absorbed less CO_3 /day than volcano samples. Not surprisingly, the blank placed in downtown Mexico City contained substantially more CO_3 than blanks set on the slopes of the volcano because of higher atmospheric pressure and higher environmental pollution levels. Isotopic evidence for atmospheric CO_2 contamination is discussed above.

Fluxes of Other Components

Analyses of fumarolic gases are often combined with COSPEC determinations of SO_2 flux in volcanic plumes to calculate fluxes of other gas components (Rose et al., 1986; Goff et al., 1994). Diffuse emissions of gas such as CO_2 sometimes found on the flanks of volcanoes (Baubron et al., 1990; Allard et al., 1991) are not accounted for in the cumulative volatile budget (10% to 40% of plume discharge at Mount Etna).

For our study, flux calculations were modified in accordance with differences due to volatile trap sampling. First, the ratios of abundances per day of Cl, CO_3 , F, As, and Hg versus SO_2 were calculated using the respective concentrations measured in the volatile trap solutions (Table DR1; see footnote 1) and assuming that total sulfur represents SO_2 . The values were then multiplied by the SO_2 flux (in metric t/day). CO_3 concentrations in caustic solutions were converted to CO_2 for the flux calculation; however, these values are too high due to contamination of the trap solutions by CO_2 from the atmosphere (discussed above).

Because COSPEC measurements were not taken during all intervals that the volatile traps were deployed (and vice versa), only the trap data for concurrent periods could be utilized. Four COSPEC measurements were obtained a few days after the eruption of December 21 and, for comparative purposes, the highest of these measurements (December 24) is correlated with trap data from December 2. Average calculated flux of five components using February, May, July, November, and December COSPEC data are listed in Table 1. The highest flux values occurred during July and December 1994, when SO_2 flux was highest.

Two sets of traps were set out on the crater rim (stations 1 and 2) for about two months in late 1995 to early 1996. An eruption of dacite lava in the summit crater and a later explosion curtailed further deployment of traps. If the data from the second set of these trap samples are combined with the SO_2 flux measured in early March 1996 (Table 1), the calculated fluxes of the other species are about 2700 t/day Cl, 270 t/day F, 1 t/day As, and 10 kg/day Hg. These values are significant, yet considerably smaller

than those correlated with much larger SO_2 emission rates in early 1997.

Fourier Transform Infrared (FTIR) Measurements

In February 1997, we conducted a series of experiments to determine chemical ratios in the volcanic plume using a modified Midac, Inc. FTIR spectrometer (Francis et al., 1996; Love et al.,

1997; Love et al., unpublished data). The instrument was used passively (i.e., without an artificial black-body light source), taking advantage of both emission and absorption spectra in the 8–12 μm and $<5 \mu\text{m}$ regions. The instrument was mounted on a tripod at a distance of 4 to 10 km from the volcano summit and a COSPEC (as described above) was mounted on an adjacent tripod to provide simultaneous SO_2 concentration and flux data. The objectives of this research in-

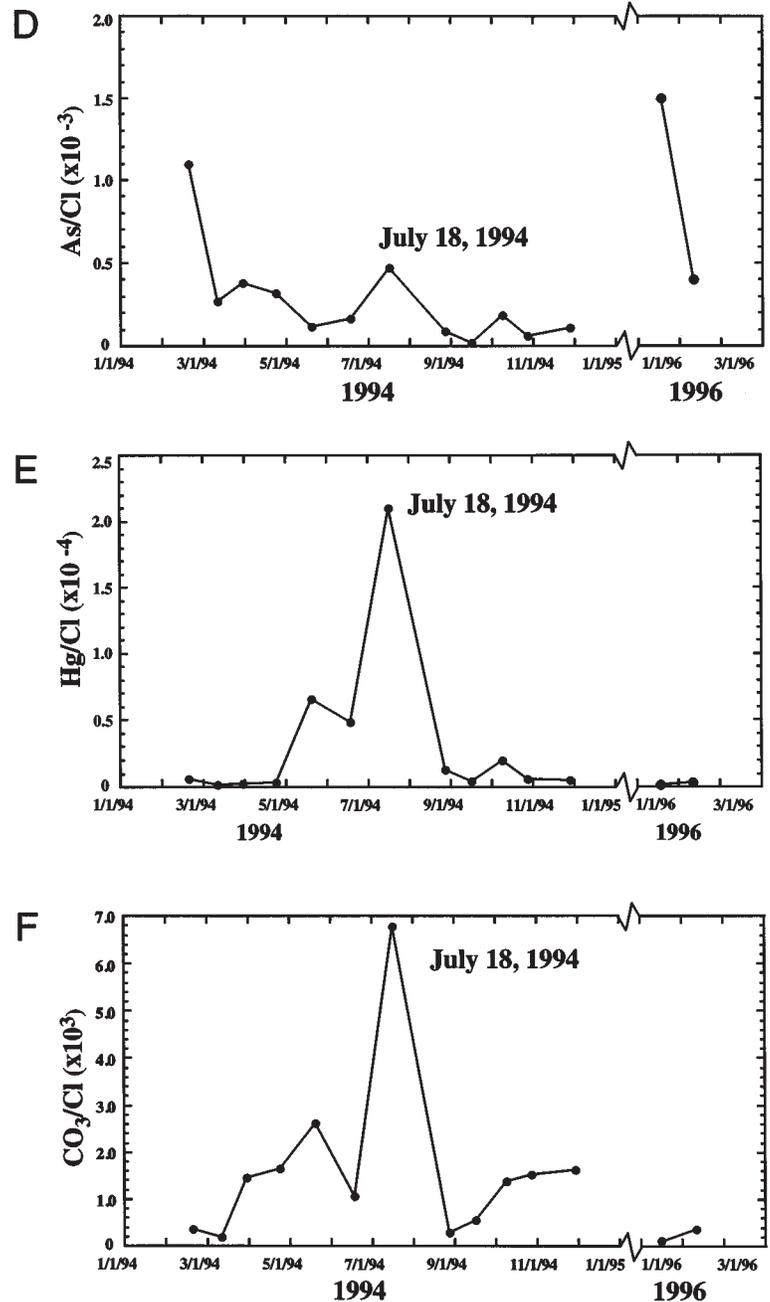


Figure 6. (Continued)

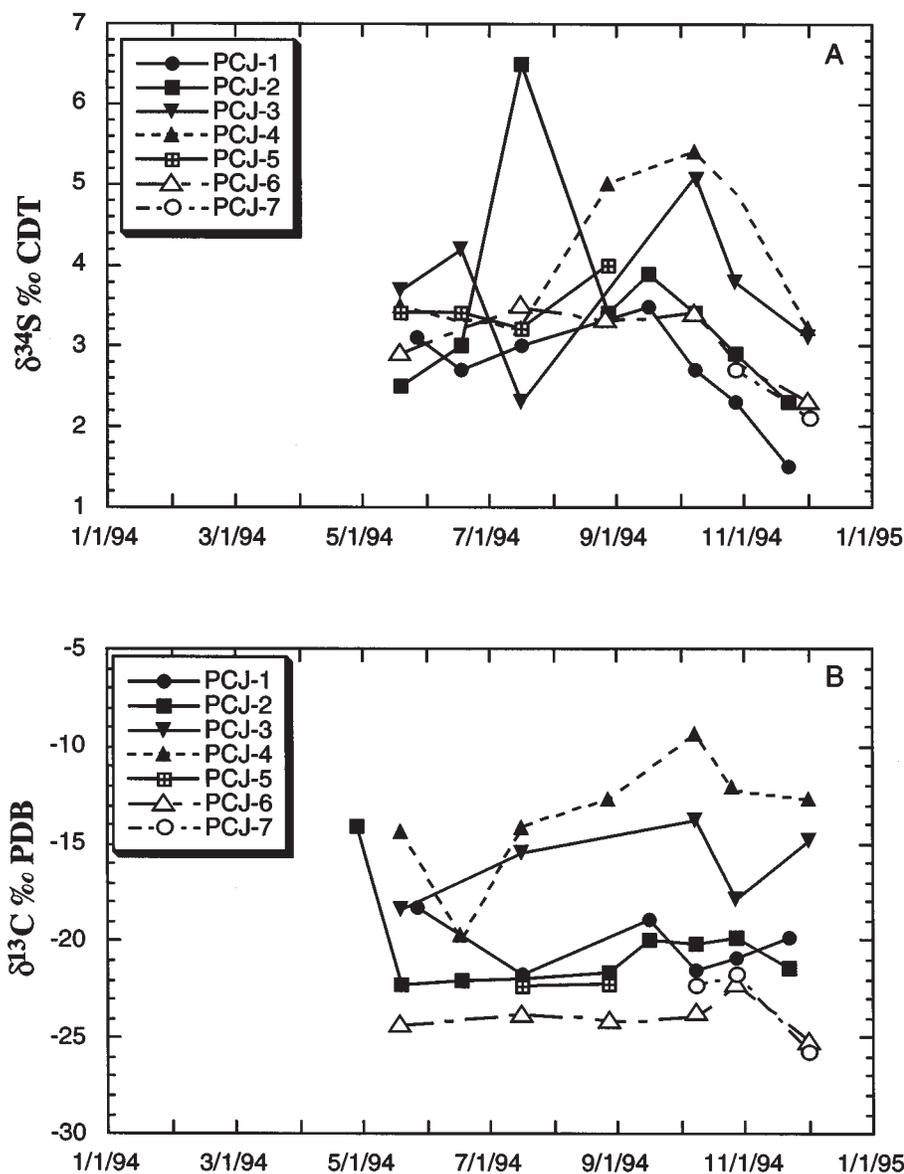


Figure 7. (A) ^{34}S isotope compositions (in per mil CDT, Canyon Diablo troilite) of total sulfur from volatile trap solutions vs. collection date. The higher $\delta^{34}\text{S}$ values observed in July follow the pronounced S pulse of around June 1994 shown in Figures 5A and 6B. All $\delta^{34}\text{S}$ values decrease sharply in late fall prior to the December eruption, corresponding to the increased flux of SO_2 . (B) ^{13}C isotope compositions (in per mil PDB, Peedee belemnite) of total carbon species in volatile trap solutions versus collection date. All values are anomalously depleted relative to air or mantle carbon due to preferential absorption of light carbon (see text). Heavier values reported for some stations at some dates may reflect a magmatic or mantle influence, but the data are not reliable for tracking volcanic eruptions.

clude development of improved remote-sensing technologies to forecast volcanic eruptions. Our quantitative FTIR measurements of HCl/SO_2 and HF/SO_2 ratios in early 1997 (Table 3) are very similar to ratios determined from volatile trap data in 1994 and 1996 and provide support for the general accuracy of both types of measurements. The data in Table 3 indicate that on some

days Popocatepetl releases more than 7000 and 1000 t/day of HCl and HF , respectively.

Flux Comparisons to Other Volcanoes

The relative proportions of the major acidic components determined at Popocatepetl are similar to those found at many passively de-

gassing volcanoes. For example, our flux values can be compared with published flux data from other calc-alkaline volcanoes (Table 4) to estimate the range of flux values expected during passive degassing and small explosive events. Each constituent shows order of magnitude variations depending on the vigor of the volcano and its unique volatile composition. Our volatile trap methods do not attempt to distinguish among sulfur species; thus, it is likely that our estimates for total sulfur released at Popocatepetl are slightly low. Sulfur released by active volcanoes tends to be more oxidized than reduced (Goff et al., 1994). Additional intervolcano comparisons are beyond the scope of this report.

During the degassing and eruptive phases of the 1990s, Popocatepetl has released an estimated total of 3.9 Mt SO_2 (through November 1996; H. Delgado, unpublished data). Using the data in Tables 1, 2, and 4, the estimated mass of the other components released during this period would be about 16 Mt CO_2 , 0.75 Mt HCl , 0.075 Mt HF , 260 t As, and 2.6 t Hg. The amount of water vapor released is roughly 200 Mt. The uncertainties on these estimates are large, about $\pm 50\%$ for the major components and higher for As and Hg. Since November 1996, the average flux of volatiles emitted from Popocatepetl has only increased. For comparison, Mount Etna, the world's largest natural emitter of SO_2 , released an average of 500 Mt H_2O and 13.4 Mt CO_2 per year from 1975 to 1995; CO_2/SO_2 averaged about 8, thus the yearly flux of SO_2 has been about 1.7 Mt (P. Allard, 1997, personal commun.). Mount Pinatubo injected 17 Mt of SO_2 into the atmosphere during the eruption of June 15, 1991 (Wallace and Gerlach, 1994).

PUBLIC HEALTH IMPLICATIONS

Our results show that Popocatepetl releases thousands of tons per day of chemically noxious gases and fumes that can have detrimental health effects on humans. The poisonous and irritating effects of SO_2 , HCl , HF , As, and Hg on respiratory passages, skin, and eyes are well documented (NIOSH, 1994); acute and chronic health risks are many (Raffle et al., 1994). We measured plume path densities by FTIR of 2000 ppm-m (SO_2), 400 ppm-m (HCl), and 50 ppm-m (HF) during our investigations in February 1997. For a plume 200 m in diameter (typical near-vent conditions) concentrations of SO_2 , HCl , and HF are 10, 2, and 0.25 mg/m^3 , respectively. These levels approach recommended exposure limits (RELs) for humans. SO_2 and HCl levels exceed those considered immediately dangerous to life and health (Table 5). Unusual meteorological and/or explosive conditions could create chemically hazardous conditions for people living near the volcano, but the

risks need further evaluation. Chemical hazards could be accentuated by a major eruption.

MAGMATIC PROCESSES

Degassing trends during 1994 (Fig. 5) show early release of CO_2 , Cl, and As with later increased release of S, F, and Hg in June and July. Decreasing $\delta^{34}\text{S}$ in SO_2 and increased emission of Cl and CO_2 relative to S, F, As, and Hg occurred prior to the eruption in December 1994. Observed variations of volatile components could result from injection of mafic magma into a convecting, more silicic chamber (Anderson, 1974); assimilation of underlying evaporite and carbonate strata, or altered volcanics, into an existing magma chamber; vaporization of acidic crater lake water and related fluids in the edifice (Rowe et al., 1992); or shallow degassing of magma during emplacement within the volcanic edifice (Gerlach, 1986). These processes are not mutually exclusive and are discussed in sequence, indicating those that we believe are most influential.

Magma Mixing

Petrologic studies of lavas and ash deposits (≤ 10 ka) from Popocatepetl, including samples of dacite from recent eruptions in 1996, reveal both chemical and textural evidence for mixing of relatively shallow silicic magma with deeper, more mafic, primitive magma (Boudal, 1985; Kolisnik, 1990; Stimac et al., 1997). Kolisnik provided the most comprehensive listing of magma mixing evidence, which includes: (1) resorbed, forsteritic olivine crystals (Fo_{90-71}), (2) reverse zoning in both clinopyroxene and orthopyroxene crystals with increases in En (enstatite fraction) of 10% to 18%, respectively, (3) plagioclase phenocrysts (An_{71-21}) showing normal and oscillatory zoning and showing evidence of resorption and regrowth with sharp calcic enrichments of 10% to 37%, (4) the occurrence of quartz and olivine together in single samples, (5) fritted plagioclase textures, and (6) orthopyroxene reaction rims on olivines. At least one lava flow shows evidence of magma mingling, i.e., light and dark magma interspersed throughout hand samples. Other samples show microscopic streaks of different groundmass colors, indicating that mixing was relatively efficient.

The features described here are classic magma mixing textures (Eichelberger, 1975; Bacon, 1986; Stimac and Pearce, 1992). As volatile-rich mafic magmas are injected into a more silicic and cooler host, the basalt is quenched and volatiles are released. This process may promote convection of the preexisting silicic magma and trigger catastrophic eruptions (Kazahaya et al., 1994; Pallister et al., 1994).

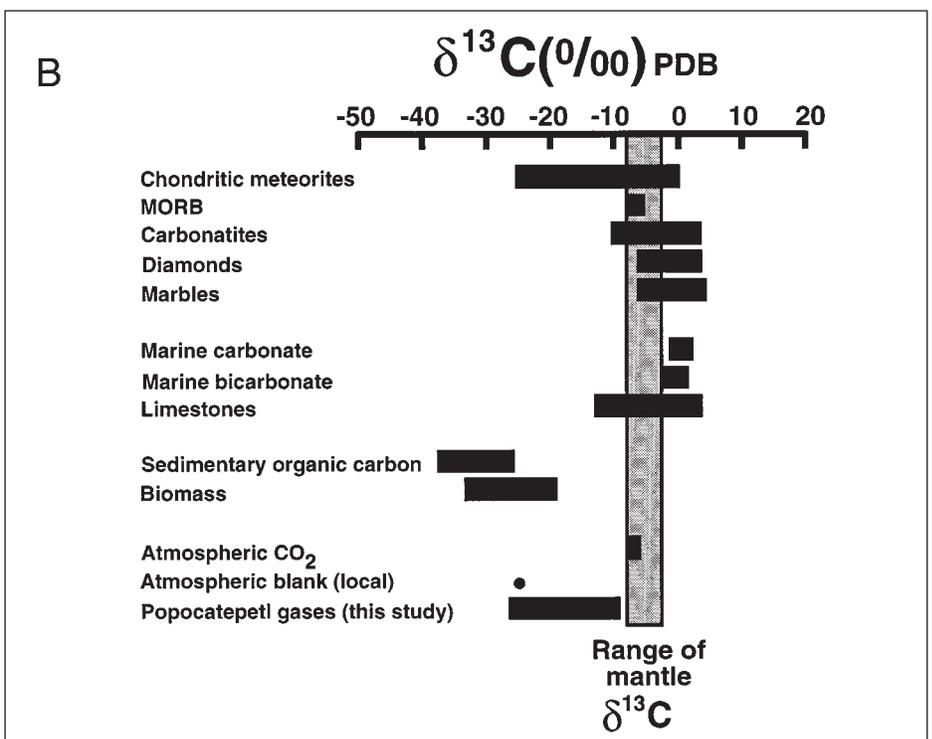
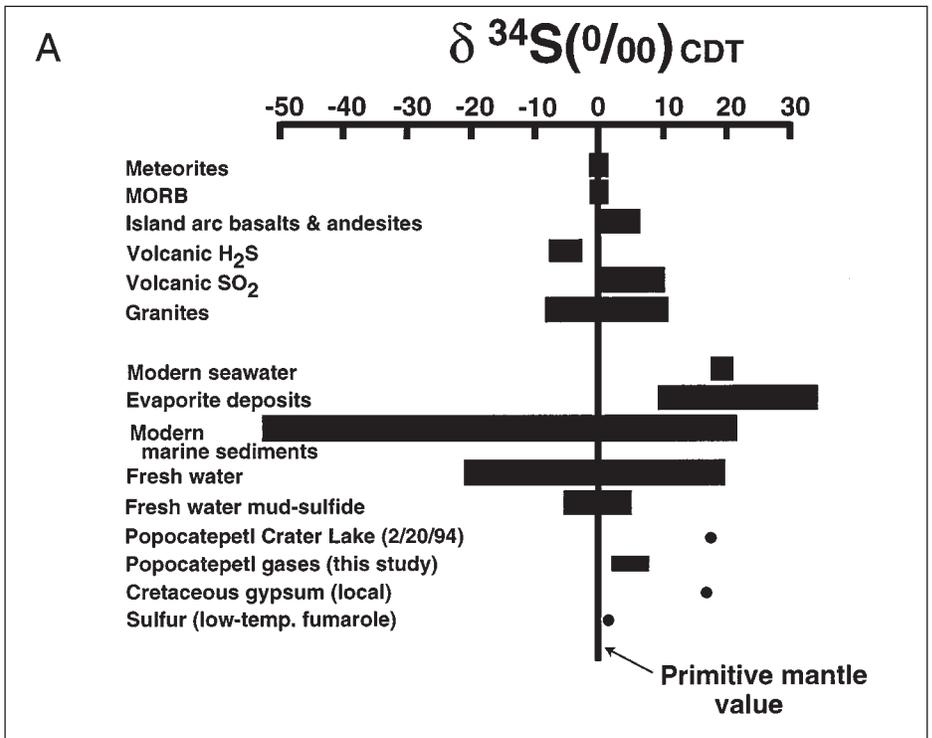


Figure 8. (A) Sulfur isotope compositions (CDT—Canyon Diablo troilite) of natural sources compared with data from this study (adapted from Rollinson, 1993). $\delta^{34}\text{S}$ values for trap samples range from 1.5‰ to 6.5‰. Values for sublimed sulfur in crater fumaroles, sulfate dissolved in the crater lake, and gypsum from underlying Cretaceous evaporites are 1.3‰, 18.6‰, and 16.4‰, respectively. MORB—mid-ocean ridge basalt. (B) Carbon isotope compositions (PDB—Peedee belemnite) of natural sources compared with data from this study (adapted from Rollinson, 1993). $\delta^{13}\text{C}$ values for trap samples range from -25.8‰ to -9.3‰. One of four blanks located outside the range of fumaroles (to measure atmospheric CO_2 contamination) yielded -24.4‰.

TABLE 1. SELECTED SO₂ FLUX RATES AND CALCULATED RATES OF OTHER VOLATILE COMPONENTS, POPOCATÉPETL VOLCANO, MEXICO

COSPEC date	SO ₂ (t/day)	Trap date	Number of stations	CO ₂ (t/day)	Cl (t/day)	F (t/day)	As (t/day)	Hg (t/day)
1994								
2/19	1200	2/20	2	<1.4 × 10 ⁴	98 ± 78	53 ± 9	0.054 ± 0.018	0.0003 ± 0.0001
5/04	900	4/10–4/30	4	<1.2 × 10 ⁵	110 ± 20	48 ± 11	0.036 ± 0.016	0.0003 ± 0.0002
7/02	3100	7/18	6	<1.1 × 10 ⁶	223 ± 34	168 ± 35	0.10 ± 0.22	0.046 ± 0.10
11/05	1260	10/28	6	<9.2 × 10 ⁴	90 ± 36	32 ± 9	0.007 ± 0.010	0.0006 ± 0.0007
12/21	Phreatic eruption							
12/23	2170							
12/24	3960	12/02	4	<5.0 × 10 ⁵	404 ± 103	125 ± 59	0.067 ± 0.098	0.003 ± 0.003
12/27	1170							
12/29	1240							
Average	~2000							
1995								
1/06	840							
1/14	530							
1/21	750							
1/28	1450							
3/10	2940							
4/03	1450							
5/24	6000							
8/08	1200							
Average	~1600							
1996								
3/07	12 900	2/11	2	<7.1 × 10 ⁵	2720 ± 142	271 ± 18	1.11 ± 0.62	0.010 ± 0.003
4/15	19 700							
5/14	11 200							
Average	~15 000							

Note: CO₂ values are too high due to atmospheric contamination. COSPEC data and average annual SO₂ are from Galindo et al. (1996) and H. Delgado, unpublished data (1997).

TABLE 2. EXPECTED CO₂ FLUX AND ESTIMATED ATMOSPHERIC CO₂ CONTAMINATION OF TRAP SAMPLES, POPOCATÉPETL VOLCANO, MEXICO

COSPEC date	SO ₂ (t/day)	Trap date	CO ₂		Atmospheric contamination	
			R = 2* (t/day)	R = 6† (t/day)	Max [‡] (%)	Min [§] (%)
2/01/94	1200	2/20/94	2400	7200	67	0
5/04/94	900	4/30/94	1800	5400	>99	46
7/02/94	3100	7/18/94	6200	18 600	>99	11
11/05/94	1260	10/28/94	2520	7560	99	60
12/21/94	Phreatic eruption					
12/24/94	3960	12/02/94	7920	23 760	99	52
3/07/96	12 900	2/11/96	25 800	77 400	98	88

*R = CO₂/SO₂ = 2 (LiCor measurements, June 1995, Gerlach et al., 1997).
†R = CO₂/SO₂ = 6 (average of GASPEC measurements, May 1996; S. Williams, unpublished data).
‡From maximum value of CO₂/SO₂ (Table 1) and R = 2.
§From minimum value of CO₂/SO₂ (Table 1) and R = 6.

In a pioneering study on melt inclusions (MI) in arc basalts (high-alumina tholeiites), Anderson (1974) found that MI in forsteritic olivine phenocrysts have considerably higher Cl values than those in more ferric olivine crystallized after eruption. Anderson proposed that undegassed mafic magmas are generally higher in Cl and S relative to water than more silicic magmas, and that Cl preferentially degasses over S at higher pressures (greater depth; e.g., Gerlach, 1986). Similar findings were reported by Metrich et al. (1993) for MI in olivines from very young alkali basalts at Mount Etna. Thus, relatively high values of Cl and low S/Cl ratios in the trap samples could be signaling periods of mafic injection into a more silicic chamber.

The data plotted in Figures 5 and 6 show relatively high Cl and low S/Cl in early and late 1994. F/Cl mimics the behavior of S/Cl. Compared to the high values in June 1994, these ratios remained at relatively low values during early 1996 and early 1997. In addition, the sulfur isotope data (Fig. 7A) show a general decrease of δ³⁴S toward more mantle-like compositions in late 1994. We argue that these trends clearly show that, except for June 1994, basalt magma has been injected into the silicic chamber beneath Popocatepetl. The possible significance of the June 1994 data is discussed in the following.

Samples of the dacite dome extruded in the crater during March 1996 display magma mixing textures: resorbed olivine (Fo₈₈₋₉₀) as well as two

pyroxenes, plagioclase, and hornblende in nearly rhyolitic glass (Stimac et al., 1997). Very few MI are found in 1996 dome olivine; therefore, MI in olivine with similar composition (Fo₈₈₋₉₀) from a Valley of Mexico basaltic andesite were also analyzed. This basaltic andesite is among the most primitive calc-alkaline lavas of the area, and most likely represents the dominant parental magma for Popocatepetl and surrounding mafic centers. Most MI in olivine from dacite and basaltic andesite are mafic (SiO₂ = 55–58 wt%; K₂O ≤ 2 wt%) in composition, 1000 to 2600 ppm S and 1400 to 1800 ppm Cl; the highest S-bearing inclusions have the highest Cl.

In contrast, MI in pyroxene from the 1996 dome are silicic (SiO₂ = 65 to 75 wt%; K₂O ≥ 3 wt%) in composition with relatively low S and moderate Cl. Major element compositions overlap with light-colored matrix glass but are generally more evolved than darker, microlite-rich matrix material, which is thought to represent hybrid melt. All silicic MI in pyroxene have Cl concentrations up to 1100 ppm; S concentrations range up to 700 ppm, but most contain about 300 ppm to below the lower limit of detection (about 50 ppm). Matrix glass ranges in composition from dacite to rhyolite; Cl is as high as 1100 ppm, and S is generally below de-

tection. These data show that the mafic end member provides considerably more Cl and S to preliminary eruption events than does the existing silicic magma.

Assimilation

Minor assimilation of volatile components from strata underlying the volcano is also a viable process. Some Holocene Popocatepetl lavas, particularly the ca. 2300 yr old Nealtican andesite flow east of the mountain, contain a variety of xenoliths ≤ 20 cm diameter (Siebe et al., 1997). Among these xenoliths are metamorphosed limestone and siliciclastic rocks partially converted to skarns (mineral assemblages of quartz + wollastonite + hedenbergite + anorthite + sphene \pm garnet and residual carbonate and sedimentary layering). Extensive pumice deposits from an eruption of Popocatepetl that occurred ca. 14 ka are also rich in lithic debris of earlier solidified magma (granitoids) and their wall rocks (metasedimentary rocks), some exhibiting contact relations. The assimilation of Cretaceous carbonates and evaporites beneath the volcano could provide additional carbon, sulfur, and other elements to the Popocatepetl magma chamber.

The impressive increases in evolution of total S and S/Cl during June 1994 suggest that another source of sulfur temporarily influenced the bulk chemistry of Popocatepetl gases. These increases correlate with the somewhat higher values of $\delta^{34}\text{S}$ obtained during mid 1994 (Fig. 7A). Because S from Cretaceous gypsum is highly enriched in $\delta^{34}\text{S}$ (+16‰) relative to mantle S, the increased $\delta^{34}\text{S}$ observed during this period could be explained by assimilation of Cretaceous wall rocks into the reactivated magma chamber. For example, if the magma initially contained only mantle S (at about 1‰ $\delta^{34}\text{S}$), then to raise the observed S-isotope value to 3.5‰ by digestion of gypsum requires that 16% of the total S comes from Cretaceous sources. If an average of 2000 t/day of SO_2 were released during 1994, then 320 t/day could originate from digestion of rocks containing gypsum. Pure gypsum contains about 19% S by weight, but gypsum-bearing strata might average only 10% S by weight. This is at least two orders of magnitude more S than contained in most basalt-to-dacite magmas (Metrich et al., 1993; Wallace and Gerlach, 1994); thus, a relatively small amount of gypsum assimilation ($\leq 1\%$) could profoundly influence the bulk S content and isotopic composition of Popocatepetl magma.

In their S-isotope study of coexisting anhydrite and sulfides in pumice from the June 1991 Pinatubo eruption, McKibben et al. (1996) showed that 23 anhydrite crystals varied in isotope compo-

sition from +3‰ to +16‰ $\delta^{34}\text{S}$. These authors concluded that not all S in Pinatubo magma was of primary origin and that some S originated from hydrothermal anhydrite or from deep degassing of earlier magma batches.

Contamination of magma by hydrothermally altered ($\delta^{34}\text{S}$ enriched) volcanics in the Popocatepetl edifice is not considered to be a realistic mechanism because xenoliths indicate that the magma chamber resides at depths well below levels of shallow alteration. As opposed to Pinatubo and many other arc volcanoes that display extensive hydrothermal alteration and have well-developed hydrothermal systems, Popocatepetl lacks both. Exposed alteration is restricted to the summit area. A geothermal assessment of thermal springs and ground waters on the lower flanks of the volcano by Werner et al. (1997) showed no magmatic contributions to these fluids and only low temperatures of equilibration ($\leq 60^\circ\text{C}$).

TABLE 3. COMPARISON OF CHEMICAL RATIOS AND FLUXES OF PLUME COMPONENTS AT POPOCATÉPETL VOLCANO, MEXICO

Date	HCl/SO ₂		HF/SO ₂		COSPEC SO ₂ (t/day)	Approximate flux	
	Trap (mass ratios)	FTIR	Trap (mass ratios)	FTIR		HCl (t/day)	HF (t/day)
1994							
2/19	0.082	N.D.	0.044	N.D.	1200	100	55
5/04	0.12	N.D.	0.053	N.D.	900	110	48
7/02	0.072	N.D.	0.054	N.D.	3100	220	170
11/05	0.071	N.D.	0.025	N.D.	1260	90	32
12/24	0.10	N.D.	0.032	N.D.	3960	400	125
1996							
3/07	0.21	N.D.	0.021	N.D.	12 900	2700	270
1997							
2/24	N.D.	N.D.	N.D.	N.D.	2000*	260	40
2/26	N.D.	N.D.	N.D.	N.D.	60 000*	7800	1100
2/27	N.D.	0.13	N.D.	0.019	13 000*	1700	250

Note: Uncertainties are generally $\pm 10\%$ – 30% (SO₂) and as much as $\pm 50\%$ (HCl and HF) if all errors are considered. N.D. = no data.

*Maximum value measured on the day given.

†Maximum values calculated assuming ratios from 2/24 to 2/27 are constant.

TABLE 4. COMPARATIVE FLUXES (T/DAY) AMONG POPOCATÉPETL AND SOME OTHER CALC-ALKALINE VOLCANOES

Method	Popocatepetl, Mexico			Galeras Colombia	Satsuma Japan	White Island New Zealand
	V. Trap	V. Trap	V. Trap	Direct	Direct	Direct
Date	7/94	12/94	3/96	1/93	10/93	5/96
H ₂ O	(150 000)*	(200 000)*	(670 000)*	10 000	13 200	38 000
SO ₂ †	3100	3960	12 900	500	450	250
H ₂ S	N.D.	N.D.	N.D.	115	8.3	215
CO ₂	12 000 [§]	16 000 [§]	52 000 [§]	2100	120	530
HCl	220	400	2700	89	120	275
HF	170	125	270	5.3	12	<1
As	0.10	0.07	1.10	1.89?	0.007	0.22
Hg	0.05	0.003	0.010	0.0004	0.0001	0.040
S (wt%)	(0.9)*	(0.9)*	(0.9)*	2.8	1.7	0.8

Note: Data from this study, Goff et al. (1994), Hedenquist et al. (1994), Christenson et al. (1996), and Goff and McMurtry (unpublished data). N.D. = no data.

*Values very approximate; assume 90% of total flux is H₂O.

†SO₂ flux by COSPEC; other values ratioed to SO₂ flux.

§CO₂ flux is average of LiCor and GASPEC values (CO₂/SO₂ = 4:1).

Vaporization of Acid Crater Lake

The summit crater of Popocatepetl contained a small, acidic lake that vanished suddenly on December 21, 1994, when ash emissions started. Contamination of magmatic volatiles with vaporized crater lake water and associated fluids in surrounding rocks could contribute some isotopically heavy sulfur to the total sulfur flux. A sample of the lake obtained in February 1994 shows that 23 660 ppm of SO₄ were dissolved in the water, along with many other major elements and metals (Table 6). The $\delta^{34}\text{S}$ -SO₄ of the lake was +18.6‰. We estimate that the lake was about 50 m in diameter and 3 m deep. If the density of the acidic water is roughly 1.2 g/cm³, then the lake contained about 55 t S. Because of the confined geometry inside the crater, we estimate that no more than two to three times the amount of acidic fluid in the lake was held within porous rocks surrounding and underlying the lake. Thus, no more than about 150 t

of isotopically heavy S was available for vaporization during the early months of 1994. Because 1000 t/day of S (or 2000 t/day SO₂) were released on average during 1994, the contribution of S from the crater lake or a shallow hydrothermal system to the total volatile output of the volcano was trivial, unless the volume of the hydrothermal system is considerably larger than our estimate.

The composition of acidic waters at the summit of Popocatépetl is similar to those at shallow hydrothermal systems in the summits and craters of many active volcanoes (Table 6). Besides temperature, such waters differ from degassing magmatic fluids in one significant way: the lake waters have interacted substantially with rocks and so contain relatively huge quantities of common rock-forming cations (e.g., Na, K, Ca, Mg, Fe, Al) as well as volatile constituents and metals (Christenson and Wood, 1993). In retrospect, analysis of some of these components in the Popocatépetl volatile trap solutions (e.g., Mg) might have indicated if vaporized crater lake water was contributed to the total volatile flux. In future monitoring efforts, trap containers should be designed to let vapors in and keep dust out. Resulting analyses could be useful in future volatile trap studies where large crater lakes occupy part of the volcano superstructure.

Substantial dissolution of rock by acidic waters happens quite rapidly. The 1996 analysis of Ruapehu crater lake water was obtained on a sample that was collected barely a month after the lake was reforming from snowmelt and degassing magmatic fluids. The previous lake had been obliterated by the eruptions of late 1995–early 1996. The crater lake inside Popocatépetl was cold and only mildly acid until the volcano reawakened in the early 1990s. By early 1994, the lake became a hot, strongly acidic brine containing abundant colloidal S. Total dissolved solids (TDS) matched those of other andesitic crater brines (Table 6).

Shallow Plug Degassing

Many experimental studies of silicate melts show that reduced pressures (and depths) allow volatile components to be released as free gas. A natural example of this process was described by Gerlach (1986), who compared shallow degassing behavior of several volatile components to magma emplacement depth and structural position within conduits and dike systems at Kilauea volcano. Although shallow emplacement of magma in the conduit of Popocatépetl will facilitate volatile degassing, COSPEC data indicate that much more SO₂ has been released than can be contained in a reasonably sized volume of near-surface dacite magma.

Eruptions since 1994 reveal that Popocatépetl tephra and extrusions contain 62–64 wt% SiO₂

(Stimac et al., 1997), very similar to Mount St. Helens dacite (Rutherford et al., 1985; Shevenell and Goff, 1993). If Popocatépetl magma contains about 4 wt% volatiles, also like Mount St. Helens dacite, then a 0.25-km-thick plug of magma ($\rho = 2.3 \text{ g/cm}^3$) in a 0.25-km-diameter conduit contains about $1 \times 10^6 \text{ t}$ of volatiles, of which 90% is probably water (Tedesco, 1995; Table 4). On the other hand, Popocatépetl released an average of 2000 t/day SO₂ for a period of at least 300 days in 1994. Because SO₂ composes no more than 5% of the total volatile phase released from most silicic volcanoes (e.g., Table 4), Popocatépetl released roughly $1 \text{ to } 5 \times 10^7 \text{ t}$ of volatiles during 1994. Since the eruption of December 1994, COSPEC measurements indicate that SO₂ flux

has jumped to values of 10 000 t/day during many periods and more than 50 000 t/day during short periods in early 1997 (Delgado and Cardenas, 1997; H. Delgado, unpublished data). Thus, it seems unreasonable that shallow plug degassing would produce the large volatile flux observed at Popocatépetl during 1994 and later.

CONCLUSIONS

Volatile trap and remote-sensing data obtained from 1994 to 1997 show that magmatic volatiles at Popocatépetl have varied substantially in their relative proportions, isotopic composition, and emission rates. Total discharge of volatiles through November 1996 was similar to yearly amounts

TABLE 5. HUMAN RECOMMENDED EXPOSURE LIMITS FOR SOME COMMON SUBSTANCES EMITTED FROM ACTIVE VOLCANOES

Substance	Exposure Limits (TWA, mg/m ³)	IDLH (mg/m ³)	Comments
CO ₂	9000	40,000	STEL = 54 000 mg/m ³
SO ₂	5	270	STEL = 13 mg/m ³
H ₂ S	C = 15	145	10 min max. peak = 75 mg/m ³
HCl	C = 7	75	N.D.
HF	2.5	30	C = 5 mg/m ³
SiO ₂	N.D.	25–50	Ca
As	C = 0.002	5	Ca
Hg	0.05 (skin)	10	C = 0.1 mg/m ³ (skin)

Note: Values are mg/m³ of air. Data are from NIOSH, 1994. See also discussions of toxic effects described in Raffle et al. (1994). Abbreviations: N.D.—no data; TWA—time weighted average, usually for a 40 hr work week; IDLH—immediately dangerous to life or health; STEL—short term exposure limit, usually a 15 min TWA; C—ceiling level that should not be exceeded at any time; Ca—carcinogenic.

TABLE 6. CHEMISTRY OF POPOCATÉPETL CRATER LAKE WATER COMPARED TO OTHER BRINES IN CRATERS OF ANDESITE VOLCANOES

	Popocatépetl	Poas	Ruapehu		White Island
	Mexico	Costa Rica	New Zealand		New Zealand
	2/20/94	3/17/90	1/26/90	5/10/96	4/29/96
Temp (°C)	>60	79	42.1	66.5	100
pH (lab)	0.86	–0.60	0.64	1.0	<0
TDS	50 880	260 000	31 040	19 240	129 200
Major and selected trace components					
SiO ₂	295	N.D.	154	494	62?
Na	1835	3080	345	650	513
K	329	2030	141	57.0	350
NH ₄	11.3	N.D.	11.2	12.5	14.1
Li	3.31	N.D.	0.20	1.02	1.81
Ca	781	170	1006	1530	2720
Mg	2520	2650	401	732	629
Sr	8.56	N.D.	N.D.	1.91	7.61
Al (total)	2110	8760	1220	638	2530
Fe	3770	5640	495	523	924
Mn	95.5	N.D.	N.D.	27.1	12.4
Cl	14 200	63 100	6551	7418	111 900
F	1150	8730	285	127	203
Br	20.2	480	10.0	11.8	<2?
SO ₄	23 660	165 000	20 400	6980	9170
PO ₄	17.8	N.D.	N.D.	4.8	<5
B	54.	N.D.	17.3	16.6	56.3
As	1.2	N.D.	1.6	1.35	3.32
Hg	0.0011	N.D.	N.D.	0.0007	2.06

Note: Values are in parts per million (ppm) unless otherwise noted. Data for Poas and Ruapehu (1990) are from Rowe et al. (1992) and Christenson and Wood (1993), respectively. Other analyses by D. Counce (Los Alamos National Laboratory). N.D.—no data. TDS—total dissolved solids.

released by Mount Etna. In early 1997, the fluxes of SO₂, HCl, and HF from Popocatepetl occasionally exceeded 50 000, 7000, and 1000 t/day, respectively. Near-vent concentrations of gases in the volcanic plume often exceeded various exposure limits for humans established by NIOSH. The results show that combined volatile trap samples and remote-sensing techniques could provide useful information for eruption forecasting, health, and safety if data are acquired quickly and systematically.

We conclude that basalt injections into an existing silicic chamber have triggered increasing activity and volatile release at Popocatepetl. Such a model is entirely consistent with the geochemical trends observed in 1994 to 1997, with the decrease of S-isotope values to more mantle-like signatures in late 1994, and with petrographic observations and melt-inclusion measurements of pre- and post-1996 lavas and tephros. The geochemical data also indicate that the evolving chamber beneath Popocatepetl assimilated minor but detectable amounts of Cretaceous wall rocks during mid-1994. The data are not explained by obliteration of the small, acid crater lake or by shallow degassing of a single batch of dacite magma injected into the conduit of the volcano.

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