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Sulfur dioxide emissions from Popocatépetl volcano (Mexico): case study of a high-emission rate, passively degassing erupting volcano

H. Delgado-Granados^{a,*}, L. Cárdenas González^b, N. Piedad Sánchez^a

^aInstituto de Geofísica, U.N.A.M. Circuito Exterior, C.U. Coyoacán, 04510 México, D.F., Mexico ^bCENAPRED, Delfín Madrigal 665, Coyoacán, 04360 México, D.F., Mexico

Abstract

Popocatépetl volcano in central Mexico has been erupting explosively and effusively for almost 4 years. SO_2 emission rates from this volcano have been the largest ever measured using a COSPEC. Pre-eruptive average SO_2 emission rates (2–3 kt/d) were similar to the emission rates measured during the first part of the eruption (up to August 1995) in contrast with the effusive–explosive periods (March 1996–January 1998) during which SO_2 emission rates were higher by a factor of four (9–13 kt/d). Based on a chronology of the eruption and the average SO_2 emission rates per period, the total SO_2 emissions (up to 1 January 1998) are estimated to be about 9 Mt, roughly half as much as the SO_2 emissions from Mount Pinatubo in a shorter period. Popocatépetl volcano is thus considered as a high-emission rate, passively degassing eruptive volcano. SO_2 emission rates and SO_2 emissions are used here to make a mass balance of the erupted magma and related gases. Identified excess SO_2 is explained in terms of continuous degassing of unerupted magma and magma mixing. Fluctuations in SO_2 emission rate may be a result of convection and crystallization in the chamber or the conduits, cleaning and sealing of the plumbing system, and/or SO_2 scrubbing by the hydrothermal system. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Sulfur dioxide emissions from Popocatépetl (5450 m), a stratovolcano in central Mexico (Fig. 1), have established new records for active volcanoes (Delgado-Granados and Cárdenas-González, 1997; Andres and Kasgnoc, 1998; Delgado-Granados, 2001). The presence of volcanic gases in magmas is the main factor governing explosive eruptions

(Heiken, 1993). Thus, gas studies in conjunction with other methods, are useful tools in better understanding the dynamics of a volcano (Tilling, 1989; Sutton et al., 1993; Andres and Rose, 1995). This is relevant considering that largely populated areas such as Mexico City (60 km from the vent) surround Popocatépetl volcano.

Geological studies show that Popocatépetl has erupted explosively in the last 15 kyr, resulting in large plinian eruptions (Siebe et al., 1996; Goff et al., 1998). One of the largest eruptions mantled a large area at 14 kyr B.P. (Siebe et al., 1995) including the area currently occupied by Mexico City. More recently, during the last 5 kyr several other plinian

^{*} Corresponding author. Tel.: +525-622-4145; fax: +525-550-2486.

E-mail address: hugo@tonatiuh.igeofcu.unam.mx (H. Delgado-Granados).

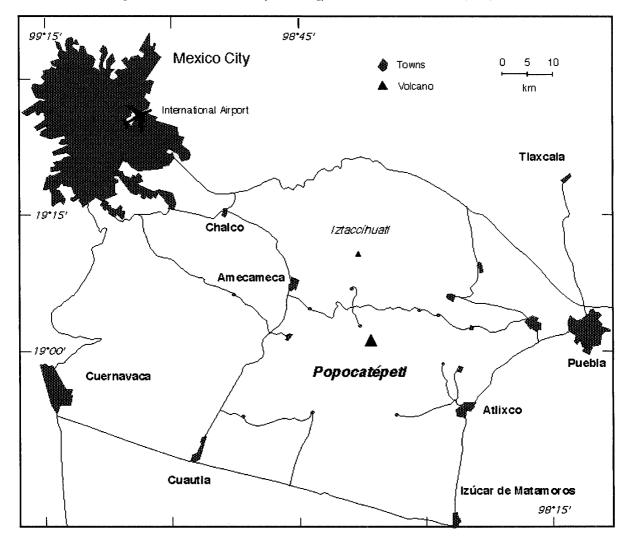


Fig. 1. Popocatépetl volcano in central Mexico. Proximity of the volcano to densely populated areas is highlighted. Main highways and roads are shown.

eruptions have occurred, devastating large areas including human settlements on the northeast flank of Popocatépetl, especially at 200 BC and 800 AD (Delgado-Granados et al., 1994a; Siebe et al., 1996).

Historic records of the eruptive history of Popocatépetl do not include a plinian eruption during the last 800 years. Records show these eruptions to be relatively 'mild' as compared with previous eruptions, and did not produce casualties or destruction of any kind (except some broken glasses and fallen fences in the 17th century). The largest eruption during the last few centuries occurred in the year 1663 and

produced some ash flows that did not reach the populated areas.

The last eruption at Popocatépetl occurred in 1920 and lasted 7 years. It consisted of several explosive events that produced eruptive columns less than 7000 masl (meters above sea level) that did not generate pyroclastic flows. A lava dome grew inside the crater in 1921 and was destroyed in 1922 by an explosive event. This eruption lasted five more years, but no documentation of additional strong explosive events exists so it is assumed that no important events occurred during the last years of the eruption.

Repose periods are about 70 years (Delgado-Granados et al., 1988). After the last eruption, the volcano remained under fumarolic conditions. The volcano showed signs of unrest since 1990, such as an increase in fumarolic activity, decrease in pH of the crater lake waters, and seismicity beneath the volcano (Delgado-Granados et al., 1994b; Werner et al., 1997; Goff et al., 1998). The current eruption began on 21 December 1994 and has lasted almost 4 years. At the time this paper was written, no clear signs of the end of the eruption could be identified.

What makes a volcano erupt violently or passively? There are many factors controlling explosivity of eruptions such as new injection of magma (Williams et al., 1986), internal build-up of pressure, magma viscosity (Sparks et al., 1997), gas content (Stix et al., 1993), and whether or not the plumbing system is sealed (Delgado-Granados, 2001). In order to recognize these processes, monitoring the behavior of SO₂ emission rates combined with other sources of information such as seismicity may be important. Regarding the gas content, SO₂ emissions give some indication of how much gas is in magmas (Wallace and Gerlach, 1994), but they may not be directly correlated to explosivity as exemplified by the large SO₂ emissions at Popocatépetl during periods of effusive eruption. Different degassing behaviors at volcanoes have led to their description as 'leaky' or 'tight' (Newhall et al., 1994). The difference between both volcano types is crucial to understanding the possible evolution of an eruption. In the case of Popocatépetl, understanding internal processes is relevant not only for scientific purposes, but also for assessment of hazards to lives and property.

This paper reports a chronology of the current eruptive episode at Popocatépetl volcano as well as a summary of sulfur dioxide emissions from 1994 until 1 January 1998. Based on this information we discuss the causes of the large emission rates at Popocatépetl.

2. Eruptive activity (1994–1998)

2.1. Onset of the eruption (December 1994)

On 21 December 1994, Popocatépetl volcano started to erupt with initial events consisting mainly

of vulcanian explosions that produced ash columns as high as 7000 masl. Individual explosions lasting 3-10 min each issued continuously from the summit for nearly a week. The ash produced during these explosions drifted towards the eastern and northeastern sectors of the volcano, falling at distances as far away as 50 km (at the city of Tlaxcala). The strongest phase of the initial eruption occurred on 24-25 December after which activity began to decline. Even though the ash column was relatively high it was not dense enough to generate pyroclastic flows due to a low eruption rate. High velocity winds present at the altitude of the ash plume efficiently lowered its density and thus, light ash fall was reported on nearby towns. During this phase, the volcano opened its conduit system after nearly 70 years of dormancy. The crater-lake nested inside the crater was emptied, but no particular morphological changes were noticed in the edifice during its initial phase of eruptive activity.

2.2. Clearing of the conduit system (January 1995–March 1996)

The explosions became intermittent during January-March 1995. The period between explosions gradually increased. Also, the volcanic plumes became poorer in ash and began to be dominated by gases. The ash mainly consisted of altered material from the old dome of 1920 or from the conduits; juvenile material was rare (<2%) and was identified by olivine crystals. These crystals are very fresh and do not show reaction rims, thus, the source is assumed to be a new and small batch of magma. The conduit system evolved into an enlarged central conduit and four new bocas at the eastern sector of the crater floor. In early August 1995, ash emissions stopped completely and other volcanic signals diminished strongly (e.g. total seismicity). The activity became so low that it was initially thought that the eruptive phase was over. This period of reduced activity persisted until March 1996.

On 5 March 1996, explosive activity resumed at Popocatépetl volcano. A large vulcanian explosion marked the beginning of the new phase by producing ash continuously for several hours. This activity later became intermittent, mirroring the eruptive activity of 1994–1995.

2.3. Explosive and effusive activity (March 1996–January 1998)

On 27 March, during a COSPEC flight over the volcano, a lava body was observed. Seismic records indicate that the lava dome likely started to be extruded on 25 March based on identified tremor signals (Global Volcanism Network Bulletin, 1996). The lava dome was extruded initially at rates between 1–3 m³/s, with maximum effusion rates of 7 m³/s during April 1996 (Delgado-Granados, unpublished data). The 5 March explosion produced elongated tongues of material, thought to be pyroclastic flows directed towards the east.

Alternating effusive and explosive activity was common during this period. Another large explosion occurred on 30 April 1996 (five climbers were killed after neglecting official warnings). The tephra erupted consisted of low to moderately vesiculated pumice clasts. The most remarkable feature was the presence of olivine crystals embedded in the pumices. Different lobes of lava were growing inside the crater and the total amount of emitted lava had grown to $8 \times 10^6 \text{ m}^3$ as of 26 May 1996 (Global Volcanism Network Bulletin, 1998a).

The lava effusion rate decayed gradually in July–August and by September 1996 the dome stopped growing. Explosions and ash emissions became less frequent but more vigorous. Strong explosions occurred on 28 October, 27 November, 5 December, and 29 December 1996. The first three did not produce strong morphological changes in the dome in spite of their intensity (the tops of some ash columns reached nearly 10,000 masl); but the last explosion destroyed the lava dome, blanketing the crater floor with rubble. Some of these explosions also produced pyroclastic flows directed towards the east and southeast.

A new lava dome started to grow between 17 and 19 January 1997. Ash emissions and explosive events decreased in intensity. Some events caused incandescent material to be expelled out of the crater, triggering fires in the nearby forest.

On 11 May, a strong explosion occurred producing an ash column that reached nearly 14,000 masl. Again, the ash consisted mainly of pumice clasts. The lava dome may have been destroyed during this explosion or during a later explosion (two other strong explosions occurred on 15 May and 14 June).

On 30 June, the strongest explosion to date occurred. The ash column reached nearly 15,000 masl high. The most striking feature of the ejected materials was the presence of two types of magma: silicic pumice of whitish color was mingled with more mafic pumice of brownish color. Vesiculation of pumices was better developed than previously observed. Olivine crystals were identified in the pumices, although crystals were not very abundant. The ash from this explosive event reached Mexico City and forced the International Airport to close. The blast was directed towards the south this time. Pyroclastic flows were observed reaching as far down the flanks of the volcano as timberline (at about 4000 m, 4 km from the crater).

Four days later, a new lava dome was observed inside the crater floor. Since no abundant fresh lava fragments were observed in the ejected material of 30 June, it is assumed that the lava dome started to grow after that large explosion. Several explosions reaching nearly 12,000 masl in altitude accompanied this new lava body. The effusion rate could not be calculated precisely but it is estimated to be larger than previous rates (>7 m³/s). In July 1996, several explosions occurred while the lava dome grew slowly.

From late July to early August 1996, the column of magma inside the central conduit subsided. This subsidence was evidenced by the appearance of circular faults facing towards the central vent and radial fractures, both affecting the dome. Explosions and volcanic tremor accompanied this event. This activity continued, and by 19 August, it was confirmed that a new lava dome was growing inside the earlier depression. The effusion rate was lower this time compared to the previous estimate. By 10 September, the new lava body almost filled the depression and by 22 October 1997 the lava emitted since 22 May 1996 was 1.5×10^6 m³. The lava emitted since 22 October through 29 November 1997 resulted in additional $1.5 \times 10^6 \,\mathrm{m}^3$ (Global Volcanism Network Bulletin, 1998a).

During November and December, the activity was distinguished by different patterns in seismic activity. Volcanic tremor accompanied the emission of new lava flows in early December. By 7 December, an additional 2.5×10^6 m³ of lava was produced (Global Volcanism Network Bulletin, 1998a) making the total amount of lava extruded from 1996 through December 1997, 13.5×10^6 m³.

On 24 December 1997, another strong explosion occurred. This explosion emitted incandescent blocks, which produced fires on the bushes surrounding the volcano. On 1 January 1998, an explosion destroyed the lava dome. This last explosion produced a crater-like depression by removing an estimated 10⁶ m³ of lava (Global Volcanism Network Bulletin, 1998a).

3. SO₂ data

3.1. Methodology

Popocatépetl volcano's activity, pre-eruptive and eruptive, has been characterized by large SO₂ emissions (Global Volcanism Network Bulletin, 1994; Delgado-Granados and Cárdenas-González, 1997). Determination of SO₂ emission rates at Popocatépetl has been made using a *Barringer* correlation spectrometer (COSPEC) model V. The methodologies used for these determinations are described by Stoiber et al. (1983), Williams-Jones and Stix (2001), Stix et al. (2001), and Delgado-Granados (2001). In fact, the measurements at Popocatépetl have challenged the established methodologies due to the enormity of the volcanic plumes (Delgado-Granados, 2001).

During the pre-eruptive phase, COSPEC measurements were carried out following Stoiber et al. (1983). Five aerial measurements were performed in 1994 using fixed-wing twin-engine planes, making five to 12 traverses beneath and perpendicular to the gas plume. Volcanic plume direction and velocity were assumed to be the same as the wind determined using air navigational GPS (Schaefer, 2001). Distances from the crater to the closest point of the traverse were commonly 9 km and not larger than 18 km.

For the eruptive phase a different methodology was utilized (Delgado-Granados, 2001). More than 350 SO₂ emission rate measurements were performed from the beginning of the eruption to 1 January 1998; 70 of them aerial measurements. In 1995, 60 emission rate measurements were made. From March 1996 to January 1998, SO₂ emission rate measurements were carried out at least two or three times per week from the ground, and from one to four aerial measurements per month.

Aerial measurements were carried out as described above. However, the emission rates were commonly very high and thus, the distances from the closest point of the traverse to the crater became larger, usually 20-25 km from the crater and as far as 55 km from the source. Usage of GPS became more important to navigate and recognize the navigation posts for the measurements, especially because distant measurements required longer traverses. This became especially crucial when the plume was directed northwest towards Mexico City where aerial measurements are restricted due to the heavy air traffic of the airport. Under those circumstances, perpendicular traverses were impossible. Therefore, alternative measurement paths were established by fixing several GPS-posts during flight.

At Popocatépetl volcano, ground-based measurements are the main way to obtain data. In order to lower operational costs, ground measurements were adopted but the methodology had to be adapted to increase accuracy (Delgado-Granados, 2001).

A fairly extensive road system exists around Popocatépetl volcano (Fig. 1) with distances to the crater no greater than 50 km. Ground-based COSPEC measurements require more calculations to obtain an SO₂ emission rate perpendicular to the plume direction. The main problem of this method is determining an accurate wind velocity (assumed to be the same as plume velocity) at the altitude of the plume (Stoiber et al., 1983). At some volcanoes, wind velocity can be obtained using an anemometer at ground level (Williams-Jones and Stix, 2001). However, at Popocatépetl volcano, wind conditions are extremely variable due to the high elevation (Delgado-Granados et al., 1995) and thus, wind conditions are completely different from the ground to the summit where the gases are exhausted into the atmosphere.

In the case of Popocatépetl volcano, wind data is obtained from aircraft approaching or leaving Mexico City airport. Normally, commercial aircraft have several navigational instruments, among them GPS. The measurements of SO₂ emission rates benefit from the proximity of the volcano to the city, because of the wind observations from pilots as they pass over the area at the same altitude as the plume. In addition, the wind data can be compared with the radiosounding data that the National Meteorological Service collects twice every day. Also, to reinforce the wind data,

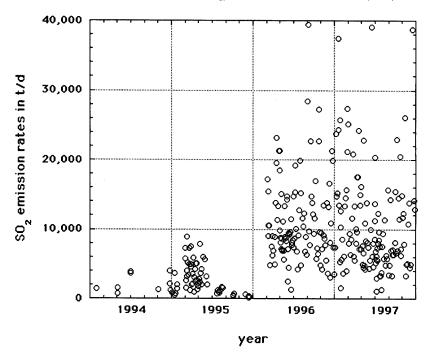


Fig. 2. Individual SO₂ emission rates per year.

estimates on the wind velocity can be made using a real-time video image of the volcano and its plume.

During aerial measurements, five to 12 traverses beneath the plume are usually made. However, during ground measurements, one to five traverses (an average of three) are made depending on the plume's width (maximum plume width could be up to 225 km). In order to have an estimate of plume dispersion in the case of ground measurements, at least one traverse is made completely from one edge of the plume to the other with an additional two to three measurements of the 'core' of the plume without the 'shoulders' (Delgado-Granados, 2001). This procedure allows having a sense on the data dispersion and an account of the total amount of SO₂ emission. For narrow plume widths, the measurement traverses always include the entire plume (Delgado-Granados, 2001).

SO₂ emission rates of the database used in this paper were carefully revised. In April 1997, a problem in the low-concentration calibration cell was found (Global Volcanism Network Bulletin, 1998b). This cell did not have the concentration given in the manufacturer's specifications, and in fact, its true

concentration was far too low. Exchanging cells and determination of the true concentration of the previously installed cell solved the problem. The instrument with the incorrect calibration cell had been used in Mexico since June 1996. Thus, the SO₂ emission measurements carried out between June 1996 and April 1997 were recalculated. Most SO₂ emission rates at Popocatépetl volcano are very high, and, therefore, the low-concentration value is not used frequently. Thus, the database did not undergo significant modifications in terms of mean SO₂ emission rates. However, some of the largest values became smaller for cases where relatively low concentrations prevailed over extremely long distances.

3.2. Results

Sulfur dioxide data are shown in Fig. 2, and summarized according to the chronology of events in Table 1. First, different periods of SO₂ emissions are identified based on the account of the eruption made earlier, i. e., periods of fumarolic, explosive, or effusive activity. Then, for every period of eruptive

Table 1 Sulfur dioxide emissions per period. Details of every period are given in the text, t = metric tons; d = days; $\sigma =$ standard deviation

| Period | Туре | Initial date | Final date | Number of days | Average SO ₂ (t/d) | σ (t/d) | Maximum (t/d) | Minimum (t/d) | Number of data | SO ₂ (t) |
|--------|-----------|--------------|------------|--------------------------|-------------------------------|------------|------------------|--------------------------|----------------|---------------------|
| 1 | Fumarolic | 01/02/94 | 20/12/94 | 322 | 2080 | 1330 | 3850 | 740 | 6 | 669,760 |
| 2 | Explosive | 21/12/94 | 30/06/95 | 191 | 3470 | 2,080 | 8910 | 530 | 50 | 662,770 |
| 3 | Fumarolic | 01/07/95 | 04/03/96 | 247 | 780 | 460 | 1660 | 12 | 15 | 192,660 |
| 4 | Explosive | 05/03/96 | 24/03/96 | 19 | 11,270 | 4470 | 17,180 | 4800 | 6 | 214,130 |
| 5 | Effusive | 25/03/96 | 29/12/96 | 279 | 11,160 | 6,170 | 39,390 | 1320 | 99 | 3,113,640 |
| 6 | Explosive | 30/12/96 | 16/01/97 | 17 | 12,930 | 7820 | 23,740 | 3520 | 5 | 219,810 |
| 7 | Effusive | 17/01/97 | 15/05/97 | 118 | 12,930 | 7,880 | 37,420 | 1560 | 45 | 1,525,740 |
| 8 | Explosive | 16/05/97 | 30/06/97 | 45 | 9910 | 8,820 | 39,100 | 4230 | 14 | 445,950 |
| 9 | Effusive | 01/07/97 | 01/01/98 | 184 | 9250 | 6450 | 38,750 | 1080 | 62 | 1,702,000 |
| | | | | | | | | Total SO ₂ em | itted: | 8,746,460 |
| | | | | | Total SO | emitted | since lava sta | rted to be extr | uded: | 7,221,270 |
| | | | Total | l SO ₂ emitte | 1997: | 6,990,020 | | | | |

or fumarolic activity an average emission rate is calculated using the available data (six to 99 measurements). Average SO_2 emission rates for periods 1 (pre-eruptive), 2 (onset of the eruption), and 3 (1995–1996 fumarolic stage) are lower than average SO_2 emission rates for periods 4–9 (explosive–effusive periods) as can be seen in Fig. 3. Pre-eruptive and onset periods yield similar SO_2 emission rates of 2–3 kt/d (1 kt/d = 1000 metric tons per day) whereas explosive–effusive periods yield averages between 9 and 13 kt/d. Fumarolic period 3 is exceptional with an average SO_2 emission rate of less than 1 kt/d.

Explosive-effusive periods do, however, show high variability. In spite of the similarity in SO_2 emissions during periods 4–9, standard deviation values are high (4–8 kt/d) and maximum values can be almost four-times larger than the average value (Fig. 3).

With these data, the total emission of sulfur dioxide can be estimated. In Table 1, the duration of every period is shown. Using the average SO₂ emission rate, we can estimate the amount of SO₂ emitted during every period. Therefore, the total SO₂ produced by the activity of Popocatépetl volcano since the pre-eruptive period in 1994 through 1 January 1998 equals nearly 9 Mt. This enormous amount of sulfur dioxide emitted over approximately 4 years is about half of the 17 Mt injected to the atmosphere by Mount Pinatubo in June 1991 (Wallace and Gerlach, 1994; Bluth et al., 1992).

SO₂ emissions are good indicators of processes

taking place at Popocatépetl volcano. SO₂ emissions are considerably larger during effusive periods due to their longer duration (Table 1). Using SO₂ emission values for every period we can construct a time-averaged cumulative curve (Fig. 4). This curve takes a notable swing after day 762 (the end of period 3 and beginning of period 4). This strong change separates a vent-clearing phase (periods 1 through 3 with average SO₂ emission rates of 2100 t/d) from an open-vent-degassing phase (periods 5–9 with average SO₂ emission rates of 11,200 t/d) with period 4 representing the end of vent- clearing activity.

Sulfur dioxide emissions at Popocatépetl volcano can be compared with lava effusion rates. Existing reports on the volume of lava produced by Popocatépetl from aerial photographs (Global Volcanism Network Bulletin, 1998a) do not coincide exactly with the chronology reported here. For comparison, we recalculated average emission rates to coincide with the periods for which lava-emission data are available (Table 2). New average SO₂ emission rates (Fig. 5) behave similarly to the last 6 periods shown in Fig. 4. Total emitted SO₂ for the period 5 March 1996-1January1998 is about 6.85 Mt, a difference of less than 2% from that obtained using data from Table 1, but subtracting the days after 7 December 1997 (the date of the last air photo). Average effusion rates per period are quite variable (0.03-4.13 m³/s), although the period between May 1996 and October 1997 comprises two lava-dome-destruction periods and

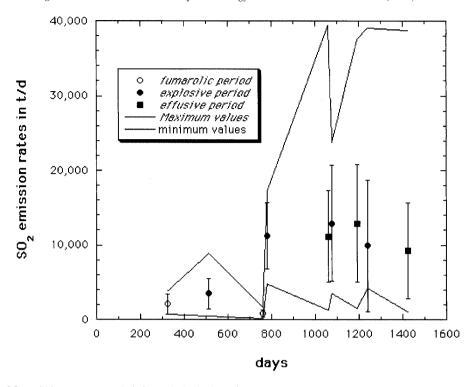


Fig. 3. Average SO_2 emission rates per period. Open circles indicate fumarolic periods, solid circles indicate explosive periods, and squares indicate effusive periods as described in the text. The data point for each period is plotted along the *x*-axis at the end of the period. Maximum and minimum SO_2 emission rates are also shown. Standard deviations are indicated with error bars. Data from Table 1.

several lava-dome-growth periods as indicated above. Therefore, this effusion rate is not as realistic as the others. Fig. 5 compares the lava effusion with sulfur dioxide emissions in a cumulative form. Cumulative SO₂ shows a steady increase during the eruption. Cumulative lava emission parallels the SO₂ trend for much of the eruption; however, the cumulative lava emission shows a much more rapid increase in the first 100 days of the eruption, and increases rapidly again after day 600.

By dividing the average mass of sulfur emitted by the mass of lava emitted, a weight percent of sulfur lost is calculated (Table 2). The mass of erupted magma was estimated assuming a lava density of nearly 2.4 g/cm³ (measured on blocks thrown by the volcano during explosive pulses). Sulfur-lost weight percent calculated values (up to 82%) are too large to have this much sulfur dissolved in magmas. Therefore, there must be another source of sulfur involved.

4. Discussion

Popocatépetl volcano SO₂ emission rates are the largest recorded for eruptive volcanoes and are, in fact, the largest measured by COSPEC (Delgado-Granados, 2001). Emission rates for the pre-eruptive and onset periods of 2-3.5 kt/d are very high as compared with emission rates from other volcanoes (Andres and Rose, 1995; Delgado-Granados, 2001). Especially high are the emission rates of the explosiveeffusive periods (9–13 kt/d). Perhaps the most striking fact is, however, that these huge emission rates have been sustained for almost 4 years. The regularity of average SO₂ emission rates through the different periods (Figs. 3 and 4) indicates that the volcano is passively degassing. Two important questions rise. What is the origin of such an amount of gas? What processes govern the changes in emission rate and produce explosions?

Total SO₂ released from Popocatépetl volcano over

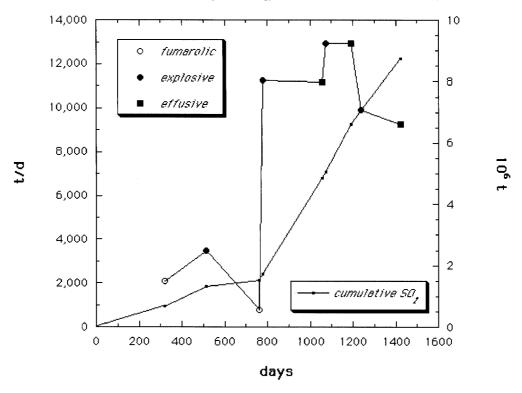


Fig. 4. Average SO₂ emission rates and SO₂ cumulative emissions. Symbols for SO₂ emission rates is similar to that of Fig. 3. Data from Table 1.

several years of activity is comparable to that released in much shorter explosive eruptions like El Chichón or Pinatubo volcanoes. The nearly 9 Mt of SO₂ emitted by Popocatépetl until 1 January 1998 is more than 50% of the SO₂ emitted by Mount Pinatubo in June 1991. Two points are worth mentioning: (a) Mount Pinatubo released its 17 Mt of SO₂ in a very short time period, whereas Popocatépetl volcano has emitted 9 Mt over 4 years; and (b) Popocatépetl is still emitting large amounts of SO₂, with no noticeable decline in passive degassing. Newhall et al. (1994) proposed the existence of two types of magmatic systems: permeable (leaky) and impermeable (tight). In this context, the high emission rates at Popocatépetl could be a consequence of a highly permeable or leaky volcanic system. Nevertheless, this does not explain the origin of excess SO₂.

Excess SO₂ is observed at Popocatépetl when total erupted magma and total SO₂ emitted are considered. Several potential sources of excess SO₂ have been proposed for other volcanoes: (a) decomposition of

anhydrite during the eruption; (b) flash vaporization of sulfate-rich hydrothermal fluids; (c) a separate vapor phase present as bubbles in the magma before eruption; (d) continuous degassing of unerupted magma in the subvolcanic reservoir; and (e) redox reactions accompanying magma mixing (Luhr et al., 1984; Andres et al., 1991; Westrich and Gerlach, 1992; Giggenbach, 1996; Gerlach and McGee, 1994; Wallace and Gerlach, 1994; Kress, 1997). Explanation (a) is unlikely at Popocatépetl because even though primary igneous anhydrite has been reported (Martin del Pozzo et al., 1996), its presence has been accidental rather than common. Explanation (b) is also unlikely at Popocatépetl due to the fact that only a poorly-developed hydrothermal system has been identified (Werner et al., 1997). Explanations (c)-(e) are not exclusive of each other and might together explain the origin of the high SO₂ emission rates from Popocatépetl volcano.

A free vapor phase present as bubbles in the preerupted magmas of Popocatépetl may explain the high

Table 2
Periods of lava production and rates compared to sulfur dioxide emission for the same periods. Equivalent mass of lava was calculated using a density of 2.4 g/cm³, sulfur dioxide percent by weight is calculated for every period of lava production. Data for lava production and effusion rates from Global Volcanism Network (1998a)

| Period | Initial date | Final date | Number of days | Volume of lava (m³) | Effusion rate (m³/s) | Average SO ₂ (t/d) | σ (t/d) | Max. (t/d) | Min. (t/d) | Number of data | SO ₂ (t) | Total mass of lava (t) | Sulfur lost (wt%) |
|--------|-------------------------------|---------------|-------------------|---------------------------|----------------------|-------------------------------------|------------|---------------|---------------|----------------|---------------------|------------------------------|-------------------------|
| A | 05/03/96 | 24/03/96 | 19 | | | 11,270 | 4470 | 17,180 | 4800 | 6 | 214,130 | 0 | |
| В | 25/03/96 | 26/05/96 | 62 | 8.00E + 06 | 1.49 | 11,130 | 5250 | 23,160 | 4960 | 28 | 690,060 | 1.91E + 07 | 1.80 |
| C | 27/05/96 | 22/10/97 | 513 | 1.50E + 06 | 0.03 | 10,690 | 6880 | 39,390 | 1080 | 179 | 5,483,970 | 3.58E + 06 | 82.00 |
| D | 23/10/97 | 29/11/97 | 37 | 1.50E + 06 | 0.47 | 10,870 | 6850 | 26,110 | 3290 | 12 | 402,190 | 3.58E + 06 | 5.60 |
| Е | 30/11/97 | 07/12/97 | 7 | 2.50E + 06 | 4.13 | 9180 | 6600 | 13,850 | 4510 | 2 | 64,260 | 5.97E + 06 | 0.50 |
| | | | | | | | | | | | 6,854,610 | 32,248,125 | |
| | Total volume of lava emitted: | | 1.35E + 07 | | | | | | | | | | |
| | | | | | | | Total So | O₂ after aj | ppearanc | ce of lava: | 6,640,480 | | |
| | | | | | | | | | Tota | l Table 1: | 6,990,020 | | |
| | | | | | | | | | Tota | l Table 2: | 6,854,610 | | |
| | | | | | | | | Di | fference | of totals: | 135,410 | 1.94% | |

SO₂ emission rates. Vapors discharged by volcanoes start to form at great depths as a continuous process of volatile exsolution from melt during magma migration (Giggenbach, 1996). Excess SO2 is likely to be derived from a pre-existing free vapor phase, which is accumulated at upper levels of a magma reservoir (Wallace and Gerlach, 1994; Gerlach and McGee, Gerlach et al., 1994; Giggenbach, 1996; 1994; Kress, 1997). In the case of blocked conduits, free vapors may accumulate until an explosive event opens the conduits, however, in the case of open conduits, the gases escape freely (Giggenbach, 1996). It is well known that arc basaltic magmas are water-rich, with as much as 6 weight percent H₂O, and together with CO2, such magmas are likely to be gas saturated at mid to upper crustal depths (e.g. Roggensack et al., 1997; Sisson and Layne, 1993; Sisson and Grove, 1993; Rose et al., 1978). As a result, basaltic magmas may degas in crustal magma reservoirs and deliver gas into overlying silicic magma bodies (Wallace, 2001). Scaillet et al. (1998) argue that arc-silicic magmas can liberate large quantities of sulfur if it is stored in a fluid phase because of the strong preference of sulfur for the fluid over the melt under oxidized conditions.

Continuous degassing of unerupted silicic magma along with new injections of mafic magma may help explain degassing patterns at Popocatépetl. As a consequence of continuous exsolution of volatiles

from unerupted magma (as suggested by Giggenbach, 1996) vapors may have accumulated at the roof of the magma chamber (Wallace and Gerlach, 1994; Gerlach and McGee, 1994) and caused the eruption of Popocatépetl in December 1994. This implies that at the time of this eruption, either no new magma or only a small batch of new magma was involved. This statement is supported by the paucity of juvenile material ejected from Popocatépetl for more than a year (<2% fresh olivine in ejected ashes), the magnitude of SO₂ emission rates, and the decreasing SO₂ emission rate pattern during the first year of the eruption. However, injections of mafic magma during 1996 caused the emission rates to increase four-fold (as suggested by the emission rates themselves and the presence of olivine in ejected pumices), and additional injections in 1997 (as suggested by textures and compositions of ejected products) made this amount of degassing sustainable. The injection of volatile-rich mafic magma into a silicic reservoir might thus be responsible for the additional amount of vapor phase and excess SO₂. Oxygen fugacity data for lavas from the surrounding region of Popocatépetl (Wallace and Carmichael, 1999) show that related basaltic magmas are more oxidized than the near FMO oxygen fugacity values considered by Kress (1997) in his proposed mechanism for the excess sulfur at volcanoes like Popocatépetl. Whether redox reactions during magma mixing were important in S release

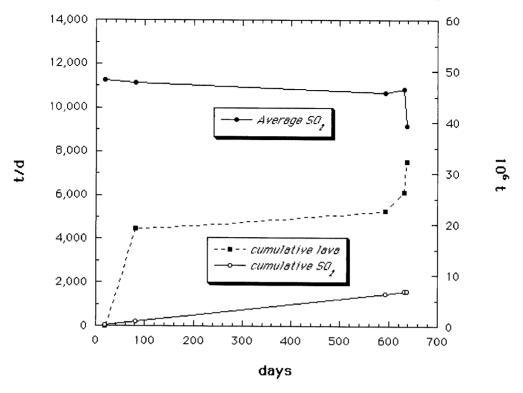


Fig. 5. Average SO_2 emissions for periods described in Table 2, cumulative SO_2 and lava emissions of SO_2 are also indicated. Notice the stability in SO_2 emissions throughout the periods. It is noteworthy that these periods may not coincide with lava dome growth but represent the times when air photographs were available to estimate volumes. Data from Table 2.

(Kress, 1997) cannot be assessed without oxygen fugacity data for both the mafic and silicic magmas involved in mixing. However, data for lavas from the surrounding region of Popocatépetl (Wallace and Carmichael, 1999) and for nearby Iztaccíhuatl volcano (Nixon, 1988) suggest little difference in oxygen fugacity of mafic and silicic magma.

How can we explain the SO₂ fluctuations and consequently the moderate explosions that have taken place at the volcano? Harris and Rose (1996) argue that decreasing gas emission rates and residual gas emissions consisting of short-lived large peaks are generated by crystallization of the magma body and episodic magma ascent and replenishment of the magma body. Average SO₂ emission rate patterns at Popocatépetl volcano are quite homogeneous in spite of their magnitude (Tables 1 and 2). However, standard deviations indicate high variability of the emissions. Decreasing pattern of average SO₂ emission rates (Table 2), and large variability of individual

emissions with peaks of nearly 40,000 t/d (Fig. 2) may reflect crystallization of a dacitic magma body and multiple episodes of mafic magma injection as in the case of Mount St. Helens (Harris and Rose, 1996). The fluctuations may also be explained in terms of processes such as convection and crystallization not only in the magma chamber but also in the conduits (Kazahaya et al., 1994; Newhall and Voight, 1998). The moderate explosions may be a result of sealing and cleaning processes of the volcano's plumbing system. Other explanations for the fluctuating patterns include scrubbing of SO₂ due to varying presence of water in the hydrothermal system (Doukas and Gerlach, 1995; Delgado-Granados and Cárdenas-González, 1997). These explanations are not mutually exclusive.

5. Conclusions

Popocatépetl volcano is a high-SO₂ emission rate,

passively degassing eruptive volcano. The sustained SO_2 emission rates of >2 kt/d for more than 4 years and >9 kt/d for more than 2 years are ample evidence for this conclusion. The SO₂ emitted during 4 years of fumarolic and eruptive activity represents 9 Mt of SO₂, roughly 50% of the amount of SO₂ released from Mount Pinatubo in June 1991 (17 Mt). In the case of Popocatépetl, release has been passive (during fumarolic periods and effusive and relatively lowmagnitude explosive eruptions) as compared to the explosive release of SO₂ at Mount Pinatubo. Excess SO₂ compared with the mass of magma erupted can be explained in terms of continuous degassing of unerupted magma (in a magma reservoir), and new injections of more mafic magma into a silicic chamber causing the sustained high emission rates. Fluctuations in SO₂ emission rates may be a result of convection and crystallization in the chamber or the conduits. along with cleaning and sealing processes of the plumbing system, and possibly some SO₂ scrubbing by the hydrothermal system.

Under these circumstances, similar magnitude explosive events may continue into the future but the occurrence of an explosive event on the scale of that at Mount Pinatubo in June 1991 is unlikely (as suggested by Kress, 1997) unless an additional injection of a large amount of mafic magma occurs. This implies that if no additional mafic magma is added, SO₂ emission rates should decline as they did during the second half of 1995 and lead to an eventual end to this eruptive episode.

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References

- Andres, R.J., Kasgnoc, A.C., 1998. A time averaged inventory of subaerial volcanic sulfur emissions. Journal of Geophysical Research 103 (D19), 25251–25261.
- Andres, R.J., Rose, W.I., 1995. Remote sensing spectroscopy of volcanic plumes and clouds. In: McGuire, W.J., Kilburn, C.R.J., Murray, J.B. (Eds.), Monitoring Active Volcanoes: Strategies, Procedures and Techniques. University College of London Press, London, England, pp. 301–314.
- Andres, R.J., Rose, W.I., Kyle, P.R., de Silva, S., Francis, P., Gardeweg, M., Moreno Roa, H., 1991. Excessive sulfur emissions form Chilean volcanoes. Journal of Volcanology and Geothermal Research 46, 323–329.
- Bluth, G.J.S., Doiron, S.D., Schnetzler, C.C., Krueger, A.J., Walter, L.S., 1992. Global tracking of the SO₂ clouds from the June, 1991 Mount Pinatubo eruptions. Geophysical Research Letters 19, 151–154.
- Delgado-Granados, H., 2001. Large volcanic-SO₂ fluxes: COSPEC measurements at Popocatepetl Volcano (Mexico). In: Hickson, C., Stix, J. (Eds.), The COSPEC Cookbook. Geological Survey of Canada (in press).
- Delgado-Granados, H., Cárdenas-González, L., 1997. Passive degassing at Volcan Popocatepetl (Mexico): 2.6×10^6 tons of SO₂ released in 617 dyas of activity. Volcanic Activity and the Environment. Abstracts. IAVCEI, Puerto Vallarta, 49.
- Delgado-Granados, H., Carrasco, N.G., Urrutia, F.J., Casanova, M., 1988. Analysis of the eruptive records of the Popocatepetl Volcano, Mexico. Kagoshima International Conference on Volcanoes. Proceedings, pp. 510–513.
- Delgado-Granados, H., Panfil, M., González, E. A., Uruñuela, G., Plunket, P., Gardner, T., Abrams, M., 1994a. Lessons from Popocatepetl Volcano (Mexico): ancient settlement buried by lavas, mudflows, and air-fall deposits. American Geophysical Union Annual Meeting, EOS, 75 (44) 737.
- Delgado-Granados, H., Williams, S.N., Fischer, T., Siebe, C., Venegas, J.J., Cárdenas, L., Wingartz, J., Orozco, G., 1994b. Popocatepetl volcano reactivated: gas monitoring shows increased fumarolic activity. II. Simposio Internacional sobre la Tectónica y el Volcanismo Cenozoicos de México, Reunión Anual de la Unión Geofísica Mexicana, 100.
- Delgado-Granados, H., Carrasco, G., Cervantes, P., Cortés, R., Molinero, R., 1995. Patrones de viento en la región del volcán Popocatépetl y Ciudad de México. In: Volcán Popocatépetl, Estudios Realizados durante la Crisis de 1994–1995, CENAPRED-UNAM, pp. 295–326 (in Spanish).
- Doukas, M.P., Gerlach, T.M., 1995. Sulfur dioxide scrubbing during the 1992 eruptions of Crater Peak, Mount Spurr Volcano, Alaska. US Geological Survey Bulletin 2139, 47–57.
- Gerlach, T.M., McGee, K.A., 1994. Total sulfur dioxide emissions and pre-eruption vapor-saturated magma at Mount St. Helens, 1980–88. Geophysical Research Letters 21 (25), 2833–2836.
- Gerlach, T.M., Westrich, H.R., Casadeval, T.J., Finnegan, D.L., 1994. Vapor saturation and accumulation in magmas of the 1989–1990 eruption of Redoubt volcano, Alaska. Journal of Volcanology and Geothermal Research 62, 317–337.
- Giggenbach, W.F., 1996. Chemical composition of volcanic gases.

- In: Scarpa, R., Tilling, R.I. (Eds.), Monitoring and Mitigation of Volcano Hazards. Springer-Verlag, Berlin, pp. 221–256.
- Global Volcanism Network Bulletin, 1994. Seismicity moderate, but distinct plume and very high SO₂ flux. 19, 13–14.
- Global Volcanism Network Bulletin, 1996. Explosion on 30 April kills five climbers near the crater rim. 21, 4.
- Global Volcanism Network Bulletin, 1998a. Cyclical dome extrusions that by late 1997 filled one-third of crater capacity. 23, 2, 8–10
- Global Volcanism Network Bulletin, 1998. Stable with moderate steam, gas, and occasional ash plumes during June. 23, 6, 6.
- Goff, F., Janik, C.J., Delgado, H., Werner, C., Counce, D., Stimac, J.A., Siebe, C., Love, S.P., Williams, S.N., Fischer, T., Johnson, L., 1998. Geochemical Surveillance of Magmatic Volatiles at Popocatépetl Volcano, Mexico. Geological Society of America Bulletin 110, 695–710.
- Harris, D.M., Rose, W.I., 1996. Dynamics of carbon dioxide emissions, crystallization, and magma ascent: hypothesis, theory and applications to volcano monitoring at Mount St. Helens. Bulletin of Volcanology 58, 163-174.
- Heiken, G., 1993. Volcanic ash: what it is and how it forms. US Geological Survey Bulletin 2047, 39–45.
- Kazahaya, K., Shinohara, H., Saito, G., 1994. Excessive degassing of Izu-Oshima volcano: magma convection in a conduit. Bulletin of Volcanology 56, 207–216.
- Kress, V., 1997. Magma mixing as a source for Pinatubo sulphur. Nature 389, 591–593.
- Luhr, J.F., Carmichael, I.S.E., Varekamp, J.C., 1984. The 1982 eruptions of El Chichón volcano, Chiapas, Mexico: mineralogy and petrology of the anhydrite-bearing pumices. Journal of Volcanology Geothermal Research 23, 69–108.
- Martin del Pozzo, A.L., Espinasa, R., Butrón, M.A., 1996. Popocatepetl's 1994–1996 activity: eruption products. EOS 77, F809.
- Newhall, C.G., Punongbayan, R.S., Gerlach, T.M., 1994. Tight and leaky volcanoes implications for forecasting explosive eruptions. Accademia Nazionale Dei Lincei 112, 13–21.
- Newhall, C.G., Voight, B., 1998. A survey of precursors to dome collapse. Colima Volcano Sixth International Meeting, 45.
- Nixon, G., 1988. Petrology of the younger andesites and dacites of Iztaccíhuatl volcano, Mexico: II. Chemical stratigraphy, magma mixing and the composition of balsatic magma flux. Journal of Petrology 29(2), 265–303.
- Roggensack, K., Herving, R.L., McJnight, S.B., Williams, S.N., 1997. Explosive basaltic volcanism from Cerro Negro Volcano: influence of volcatiles on eruptive style. Science 277, 1639– 1642.
- Rose, W.I., Anderson, A.T., Woodroof, L.G., Bonis, S.B., 1978. The October 1974 basaltic tephra from Fuego Volcano: description and history of the magma body. Journal of Volcanology Geothermal Research 4, 3–53.
- Scaillet, B., Clemente, B., Evans, B.W., Pichavant, M., 1998. Redox control of sulfur degassing in silicic magmas. Journal of Geophysical Research 103 (B10), 23937–23949.
- Schaefer, S.J., 2001. Navigation aspects of airborne correlation spectrometer (COSPEC) determinations of sulfur dioxide flux from volcanoes. In: Hickson, C., Stix, J. (Eds.), The COSPEC Cookbook. Geological Survey of Canada (in press).

- Siebe, C., Abrams, M., Macías, J.L., 1995. Derrumbes Gigantes, Depósitos de Avalancha de Escombros y Edad del Actual Cono del Volcán Popocatépetl. In: Volcán Popocatépetl: Estudios Realizados Durante la Crisis de 1994–1995. CENAPRED-UNAM, pp. 195–220 (in Spanish).
- Siebe, C., Abrams, M., Macías, J.L., Obenholzner, J., 1996. Repeated volcanic disaster in prehispanic time at Popocatepetl, Central Mexico: pasta key to the future? Geology 24, 399-402.
- Sisson, T.W., Grove, T.L., 1993. Experimental investigations of the role of H₂O in calc-alkaline differentiation and subduction zone magmatism. Contributions to Mineralogy and Petrology 113, 143–165
- Sisson, T.W., Layne, G.D., 1993. H₂O in basalt and basaltic andesite glass inclusions from four subduction-related volcanoes. Earth and Planetary Science Letters 117, 619–635.
- Sparks, R.S.J., Bursik, M.I., Carey, S.N., Gilbert, J.S., Glaze, L.S., Sigurdsson, H., Woods, A.W., 1997. Volcanic Plumes, John Wiley & Sons Ltd, Chichester, England, 574 pp.
- Stix, J., Zapata G., J.A., Calvache V., M.L., Cortés J., G.P., Fischer, T.P., Gómez M., D., Narváez M., L., Ordóñez V., M., Ortega E., A., Torres C., R., Williams, S.N., 1993. A model of degassing at Galeras volcano, Colombia, 1988–1993. Geology 21, 963–967.
- Stix, J., Williams-Jones, G., Hickson, C., 2001. Applying the COSPEC at active volcanoes. In: Hickson, C., Stix, J. (Eds.), The COSPEC Cookbook. Geological Survey of Canada.
- Stoiber, R.E., Malinconico Jr, L.L., Williams, S.N., 1983. Use of the correlation spectrometer at volcanoes. In: Tazieff, H., Sabroux, J.C. (Eds.), Forecasting Volcanic Events. Developments in Volcanology. Elsevier Science Publisher, The Netherlands, pp. 425–444.
- Sutton, A.J., McGee, K.A., Casadevall, T.J., Stokes, J.B, 1993.
 Fundamental volcanic-gas-study techniques: an integrated approach to monitoring". In: Ewert J.W., Swanson (Eds.), Monitoring Volcanoes: Techniques and Strategies Used by the Staff of the Cascades Volcano Observatory, 1980–90. US Geological Survey Bulletin 1966, pp. 181–188.
- Tilling, R.I., 1989. Introduction and Overview. In: Tilling, R.I. (Ed.), Volcanic Hazards. Short course presented at the 28th International Geological Congress. American Geophysical Union, Washington DC, pp. 1–8.
- Wallace, P.J., 2000. Volcanic emissions and the abundance and distribution of exsolved gas in magma bodies. Journal of Volcanology and Geothermal Research, this volume.
- Wallace, P.J., Gerlach, T.M., 1994. Magmatic vapor source for sulfur dioxide released during volcanic eruptions: evidence from Mount Pinatubo. Science 265, 497–499.
- Wallace, P.J., Carmichael, I.S.E., 1999. Quaternary volcanism near the Valley of Mexico: implications for subduction zone magmatism and the effects of crustal thickness variations on primitive magma compositions. Contributions to Mineralogy and Petrology 135, 291–314.
- Werner C., Janik, C., Goff, F., Counce, D., Johnson, L., Siebe, C., Delgado-Granados, H., Williams, S., Fischer, T., 1997. Geochemistry of summit fumarole vapors and flanking thermal/mineral waters at Popocatépetl volcano, Mexico. Los

Alamos National Laboratory, Series report LA-13289-MS, 33 pp.

Westrich, H.R., Gerlach, T.M., 1992. Magmatic gas source for the stratospheric SO cloud from the June 15, 1991, eruption of Mount Pinatubo. Geology 20, 867–870.

Williams, S.N., Stoiber, R.E., García, N.P., Londoño, A.C., Gemell,

B.J., Lowe, D.R., Connor, C.B., 1986. Eruption of the Nevado del Ruíz Volcano, Colombia, on 13 November, 1985: Gas flux and fluid chemistry. Science 233, 964–967.

Williams-Jones, G., Stix, J., 2001. Using the COSPEC in the Field. In: Hickson, C., Stix, J. (Eds.), The COSPEC Cookbook. Geological Survey of Canada.