

Chapter 3

Applying the COSPEC at Active Volcanoes

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1. INTRODUCTION

The previous chapter discussed how to make COSPEC measurements. The purpose of this chapter is to illustrate how the measurements are interpreted and used in explaining a volcano's activity. To accomplish this, we discuss case histories of volcanoes for which a sufficiently large COSPEC database has been established. Our objective is for the reader to use these case histories as a guide in interpreting the activity of volcanoes which he or she is monitoring. The chapter thus serves both as a summary and synthesis of what is known and also as a practical guide for interpreting volcanic activity.

This chapter consists of four principal sections. The first section examines the behavior of sulphur in magmatic, hydrothermal, and atmospheric environments, i.e., as gas rises from magma within the crust, passes through the Earth's surface, and mixes with the atmosphere. The second section is a data compilation of sulphur emissions from volcanoes. The third section, which represents the bulk of the chapter, examines case histories of COSPEC measurements at active volcanoes. The fourth and final section discusses selected techniques which can be used in conjunction with the COSPEC.

2. THE BEHAVIOR OF SULPHUR IN MAGMATIC, HYDROTHERMAL, AND ATMOSPHERIC ENVIRONMENTS

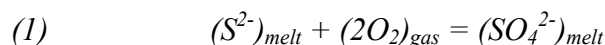
In this section, we examine the behavior of sulphur and SO₂ as magma evolves, ascends, and erupts. We first look at experimental evidence bearing on sulphur speciation and solubility in magmas. We then consider the role of shallow hydrothermal systems as they interact with a rising magma, and the implications in terms of sulphur. Lastly, we discuss how SO₂ is dispersed, oxidized, and fractionated once it is injected into the atmosphere by volcanic activity.

2.1. Magmatic sulphur: solubility, redox state, and concentrations

While many advances have been made during the past twenty years in understanding the behavior of sulphur in magmatic systems, certain problems also remain. In this section we outline some of what is known about sulphur behavior, and we raise some questions concerning what is not known. The information is largely taken from the excellent compilation by Carroll and Webster (1994).

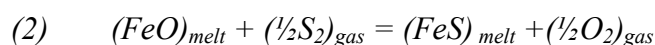
Figure 1 shows fugacities of different sulphur gas species as a function of oxygen fugacity, as defined by the departure from the fayalite-magnetite-quartz (FMQ) buffer. For a C-S gas, SO₂ is the dominant species at ΔFMQ higher than -1 to -2, followed by SO. At ΔFMQ lower than -1 to -2, COS and S₂ are dominant, followed by SO₂. For a geologically more realistic H-C-S gas, SO₂ is still dominant at ΔFMQ higher than -1 to -2. At ΔFMQ values lower than these, H₂S is now dominant, followed by COS and S₂, and SO₂ is a minor species.

When sulphur dissolves in a silicate melt, it does so either in the form of sulphide under reducing conditions or as sulphate when conditions are more oxidizing:

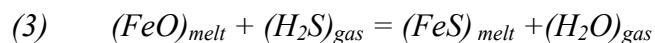


Sulphide is stable at $f(\text{O}_2)$ values lower than FMQ. Dissolved sulphur in the form of sulphate becomes significant at ΔFMQ values higher than +1.

Under reducing conditions, the amount of iron in the melt plays an important role. For anhydrous melts:



For hydrous melts:



These equations show that under reducing conditions, increasing iron in a silicate melt will promote higher sulphur solubilities. These relations indicate that sulphur solubility also will depend on $f(\text{S}_2)$, $f(\text{O}_2)$, and $f(\text{H}_2\text{O})$.

Under oxidizing conditions where dissolved sulphur is present largely as sulphate, the amounts of alkaline earth (e.g., Ca) and alkali elements in the melt may influence sulphur solubility in a way similar to iron in a reducing melt, but these relations are not clear.

When a silicate melt becomes saturated in sulphur, sulphur-rich phases appear. Under reducing conditions, an iron sulphide mineral (e.g., pyrrhotite) or immiscible sulphide melt forms. The sulphide phase can remove iron from

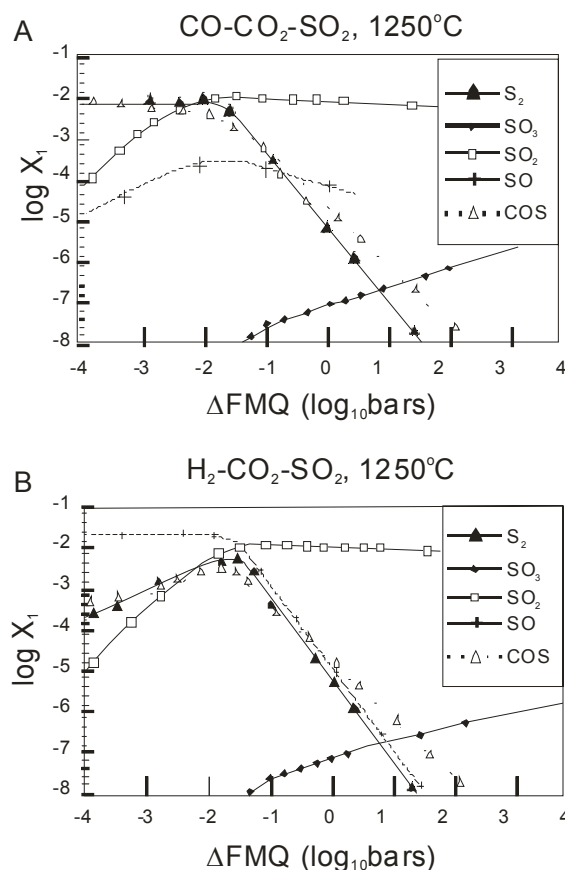


Fig. 1. Calculated gas fugacities of various sulphur species as a function of oxygen fugacity, as expressed by ΔFMQ , which represents the difference in oxygen fugacity from the fayalite-magnetite-quartz (FMQ) equilibrium. Conditions are 0.1 MPa total pressure, 1250°C, and constant 2.1 vol. % SO₂ in the inlet gas mixture. (a) CO-CO₂-SO₂ gas mixture. (b) H₂-CO₂-SO₂ gas mixture. From Carroll and Webster (1994).

the silicate melt, thereby reducing sulphur solubility in the silicate melt. Under highly oxidizing conditions ($\Delta\text{FMQ} > 1.5$), anhydrite precipitates. If the melt is not saturated in sulphur, the sulphur still can be removed from the melt by partitioning into a C-H-O-rich fluid phase.

Figure 2a shows sulphur behavior in sulphur-undersaturated natural melt compositions where no sulphur-rich phase is present. Salient points to be drawn from this diagram include the following:

- Sulphur solubility reaches a minimum at ΔFMQ between 0 and +1.
- As one moves away from this minimum, sulphur solubility appears to increase more rapidly under reducing conditions compared to oxidizing, although this relation is not entirely clear.
- Mafic melts reach a maximum of 1,000-1,600 ppm sulphur at ΔFMQ between -4 and -5.
- Perhaps most importantly, the amount of iron in the melt strongly influences the sulphur solubility, with iron-rich melts such as hawaiite and tholeiite having significantly higher sulphur solubilities compared to the iron-poor rhyodacite. This is particularly noticeable under highly reducing conditions where the solubilities for the iron-rich and iron-poor melts diverge considerably.
- Under oxidizing conditions, felsic melts have very low sulphur solubilities, probably since they are iron-poor.

The minimum in sulphur solubility shown in Figure 2a indicates that sulphur concentrations dissolved in magma will be very low at this level of oxygen fugacity. This is observed for back arc basin lavas erupted in deep submarine environments (Nilsson and Peach, 1993). In this case, sulphur concentrations vary from 100 ppm to 1,900 ppm, with most samples below 1,100 ppm. Nilsson and Peach (1993) suggest that the sulphur contents are controlled by vapor-melt equilibria, i.e., deep degassing. Another study by Kress (1997) suggests that mixing of a reduced, sulphide-saturated basalt with an oxidized, anhydrite-saturated dacite before the 1991 Mt. Pinatubo eruptions produced a sulphur-undersaturated andesite with oxygen fugacity at or near the minimum in sulphur solubility. Since the sulphur solubility declined, the large amounts of sulphur formerly present in the dacite and basalt were forced to exsolve from the hybrid andesite into a gas phase.

On the other hand, work on alkaline magmas has shown that sulphur concentrations and solubilities can be high, with sulphur ranging from 1,000 ppm to 4,000 ppm, despite oxygen fugacities near the solubility minimum (Metrich and Clocchiatti, 1996). Apparently, factors such as high alkali contents, low silica contents, elevated pressure-temperature conditions, and/or water-rich compositions can enhance the solubility of sulphur at these oxidation levels.

By contrast with undersaturated conditions, sulphur solubility in high-temperature, sulphur-saturated trachyandesite melt is elevated when anhydrite is present (oxidizing) and comparatively low when sulphide is present (reducing) (Fig. 2c). While the reasons for these relationships are not fully clear, the transfer of iron from the silicate melt to the sulphide phase under reducing conditions may result in lowered sulphur solubility. At low temperatures and pressures, such melts show low sulphur solubility (Fig. 2d). This diagram clearly shows that sulphur solubility is very sensitive to changes in both pressure and temperature under oxidizing conditions.

Volcanoes such as Mt. Pinatubo release large amounts of SO_2 explosively, yet electron microprobe analyses of melt inclusions and matrix glasses reveal very low sulphur concentrations, frequently less than 100 ppm. The presence of anhydrite in the dacitic eruptive

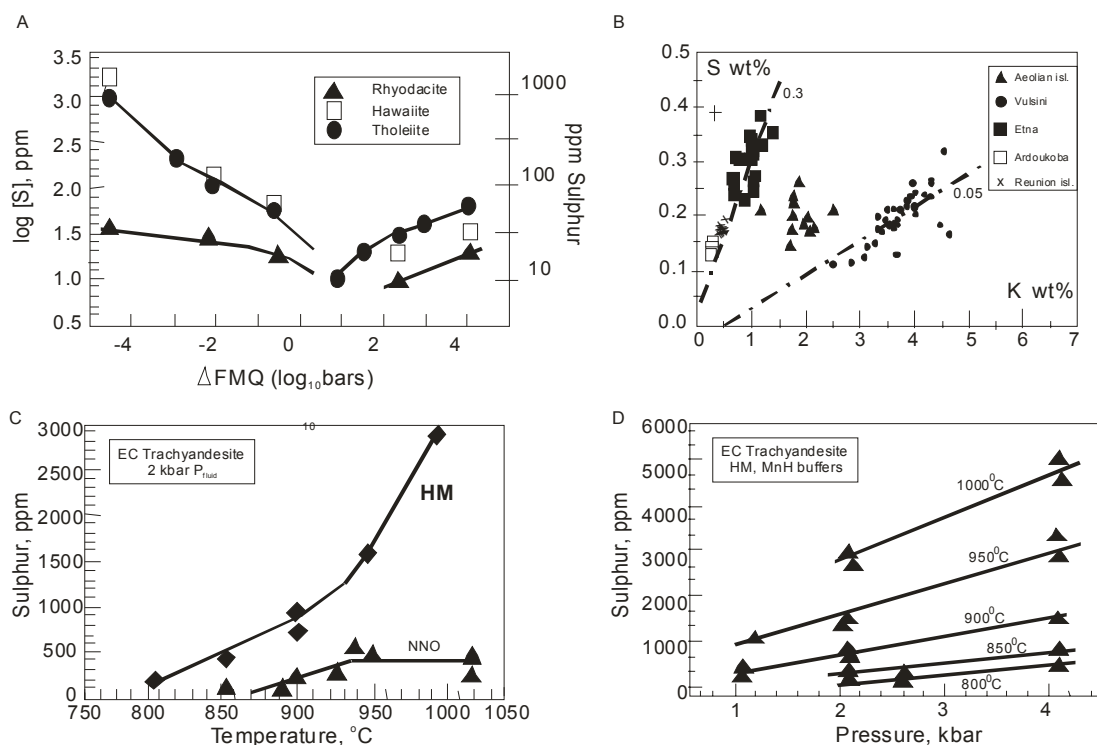


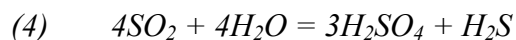
Fig. 2. (a) Sulphur solubility in sulphur-undersaturated tholeiite (11.75 wt.% FeO*), hawaiiite (13.1% FeO*), and rhyodacite (3.0% FeO*) melts as a function of oxygen fugacity, expressed by ΔFMQ . Conditions are 1250 $^{\circ}C$ and 2.1 vol.% SO_2 in the gas inlet mixture. From Carroll and Webster (1994). (b) Plot of potassium vs. sulphur concentrations in melt inclusions from various alkaline rock series. Filled triangles: shoshonitic basalts from Vulcano and Stromboli volcanoes, Aeolian island arc, Italy; filled circles: potassic rocks from Vulcini volcano, Italy; filled squares: hawaiiites and basalts from Mt. Etna, Italy; open squares: tholeiites from Ardoukoba, Afar, Ethiopia; crosses: transitional basalt, Piton de la Fournaise, Réunion Island. From Metrich and Clocchiatti (1996). (c) Sulphur solubility in sulfur-saturated trachyandesite melt as a function of temperature at 200 MPa total pressure. All samples coexist with a H-O-S fluid phase. The line marked HM indicates oxygen fugacity at the HM buffer, and sulfur saturation is marked by the presence of anhydrite. The line marked NNO indicates oxygen fugacity at the NNO buffer, with sulphur saturation marked by the presence of pyrrhotite or an immiscible sulfide melt. From Carroll and Webster (1994). (d) Sulphur contents as a function of pressure and temperature in anhydrite-saturated trachyandesite. The experiments were run at or near the HM and MnH buffers. Note the very low sulfur concentrations at low temperatures and pressures (<500 ppm) and the very high concentrations at high temperatures and pressures (>3,000 ppm). From Carroll and Webster (1994).

products of Mt. Pinatubo suggests sulphur saturation under oxidizing conditions, yet the very low sulphur and iron contents in the evolved rhyolitic glasses imply low sulphur solubilities. The low solubilities suggest that the dacitic magma was stored at low pressures and/or temperatures before the eruption.

2.2. The role of hydrothermal systems

As magmatic gas is released from magma, it reacts with surficial and meteoric waters on and within the edifice of a volcano. The result is the development of a hydrothermal system which may serve as an envelope and buffer zone between the magma and the surface. Hydrothermal systems are characterized by the presence of acid-sulphate assemblages, zones of alteration or extensive leaching, crater lakes, native sulphur deposits, fumarole fields, etc. Volcanic hydrothermal systems logically should be better developed in environments which have abundant sources of water (e.g., wet climates, snow, ice). Oppenheimer (1996) has divided

volcanoes into 'dry' and 'wet' types. Dry volcanoes are those that have poorly developed hydrothermal systems and thus degas persistently through open vents (e.g., Mt. Etna, Arenal, Masaya). Wet volcanoes have well-developed hydrothermal systems (e.g., Mt. Pinatubo, Nevado del Ruiz) which can absorb magmatic SO₂ through the reaction:



By this process of absorption, sulphur can be retained within a volcano, rather than released to the atmosphere. This retention process is best exemplified by acid crater lakes which absorb volcanic gas. Examples include Poás in Costa Rica (Rowe et al., 1995), Mt. Pinatubo in the Philippines (Campita et al., 1996), and Soufrière St. Vincent in the Lesser Antilles (Sigurdsson et al., 1977). When crater lakes are present, SO₂ fluxes are normally very low. When the lakes dry up, gases are no longer absorbed and SO₂ fluxes consequently increase. A similar phenomenon can be observed at Vulcano in Italy, where high-temperature acid gases (including SO₂) are emitted from the central crater, while boiling-point fumaroles (100°C) on the beach have been neutralized and depleted of acid gas by the "washing" action of meteoric and seawaters (Chevrier and Le Guern, 1982).

Absorption of SO₂ also is believed to have taken place during the 1991-1993 reactivation of Mt. Spurr volcano in Alaska (Doukas and Gerlach, 1995). The activity of Mt. Spurr was centred on Crater Peak. During times of quiescence between explosive eruptions, SO₂ fluxes measured by COSPEC were usually less than 100 metric tonnes per day (t d⁻¹) (Fig. 3). A strong H₂S odor frequently was present, and CO₂/SO₂ ratios were 10-100. Furthermore, there was a four-fold increase of sulphate concentrations in the summit crater lake between August 1970 and June 1992. SO₂ fluxes were high only during and after the 1992 explosive eruptions; the TOMS

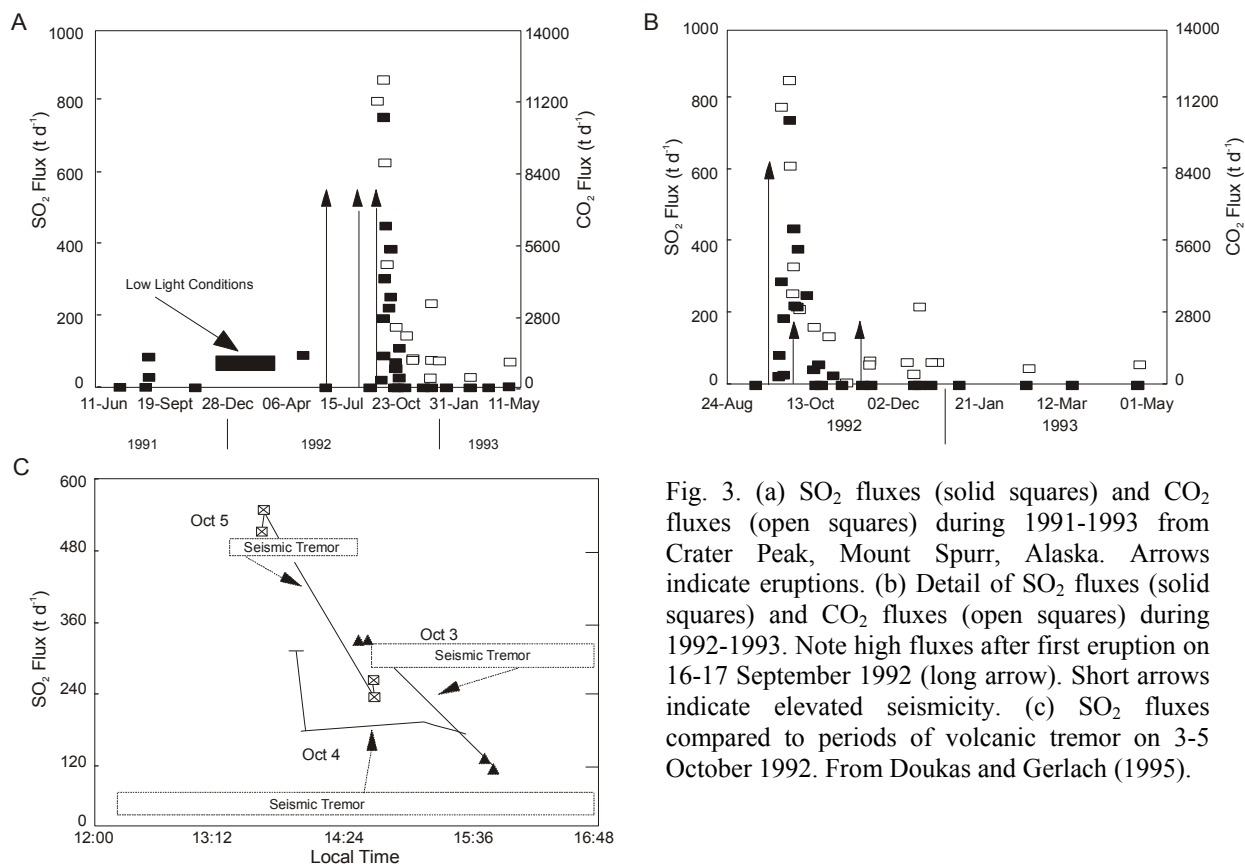


Fig. 3. (a) SO₂ fluxes (solid squares) and CO₂ fluxes (open squares) during 1991-1993 from Crater Peak, Mount Spurr, Alaska. Arrows indicate eruptions. (b) Detail of SO₂ fluxes (solid squares) and CO₂ fluxes (open squares) during 1992-1993. Note high fluxes after first eruption on 16-17 September 1992 (long arrow). Short arrows indicate elevated seismicity. (c) SO₂ fluxes compared to periods of volcanic tremor on 3-5 October 1992. From Doukas and Gerlach (1995).

satellite measured a total of 830,000 tonnes of SO₂ emitted by the three explosive eruptions, and COSPEC measurements recorded values up to 750 t d⁻¹ after the 16-17 September 1992 eruption (Fig. 3b). By contrast, passive non-eruptive degassing emitted only 6,000 tonnes. For comparison, the 1989-1991 activity at Redoubt volcano (also in Alaska) emitted about 175,000 tonnes of SO₂ explosively and 800,000 tonnes SO₂ passively (Casadevall et al., 1994).

The low SO₂ emissions from passive degassing at Crater Peak are believed to be the result of SO₂ absorption by the hydrothermal system within a permeable edifice, with surficial snow and ice the source of water (Doukas and Gerlach, 1995). Large amounts of SO₂ were released by explosive degassing when pathways were open, allowing direct release of SO₂ from the magma to the atmosphere. Additionally, the hydrothermal system may have boiled during the eruptions, releasing H₂S which may have then been oxidized to SO₂. As a last point, the 16-17 September eruptions were followed by tremor episodes on 3-5 October, which are believed to be a manifestation of boiling as water recharge occurred in the dry-out zone. During these tremor episodes, SO₂ fluxes declined (Fig. 3c), which may be indicative of SO₂ absorption by the hydrothermal system as it boiled (Doukas and Gerlach, 1995).

If hydrothermal systems can store sulphur, is the sulphur subsequently remobilized? Oppenheimer (1996) has suggested that hydrothermal sulphur can be remobilized during explosive eruptions, which could account for the excess sulphur emissions of many volcanoes. If boiling of the hydrothermal system occurs during an explosive eruption, H₂S is released, not SO₂. Some of the H₂S may be subsequently oxidized to SO₂. Decomposition of pyrite also may produce SO₂ (Oppenheimer, 1996).

2.3. *SO₂ - SO₄ conversion in gas plumes*

For reduced hydrous magmas which are gas-saturated, the sulphur in the gas phase is largely in the form of H₂S and/or SO₂ (see above). By contrast, there is general agreement that sulphur in an eruption column consists mainly of SO₂. These observations imply that under most conditions, the H₂S initially present is rapidly oxidized to SO₂ during the eruption.

With time, SO₂ in a volcanic gas column is oxidized and converted to sulphuric acid. The nature of SO₂ conversion depends upon a number of factors which influence the rate and amount of oxidation to varying degrees. In this section we summarize the different types of oxidation reactions which should be considered for a volcanic gas plume. This summary draws on the recent synthesis by Eatough et al. (1994) and examines some of the gaps in our understanding of oxidation processes.

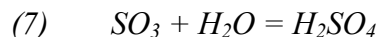
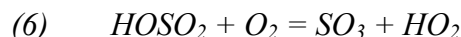
Oxidation of SO₂ can be considered in terms of three major processes:

- (1) *homogeneous reactions*: these types of reactions occur in the gas phase and depend mainly on temperature and relative humidity. The amount of SO₂ that is oxidized is generally small, less than 10-15% SO₂/hour.
- (2) *aqueous phase reactions*: these reactions occur in the presence of clouds and fog, where SO₂ is dissolved and converted in aqueous solution. The rate of SO₂ oxidation depends upon the size of the moisture droplets and the concentrations of the principal oxidants (O₃, H₂O₂). These reactions may be significant when a volcano's summit is surrounded by cloud and fog.
- (3) *heterogeneous reactions*: these reactions take place on ash particles, which can remove SO₂ from the gas phase. They are probably important when ash is emitted, but they are not well understood.

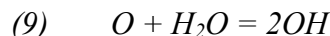
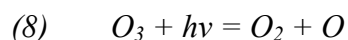
We now examine some details of these various processes.

2.3.1. Homogeneous reactions

In the gas phase, SO_2 is converted to sulphuric acid by the following three reactions:



In this manner, sulphur is oxidized from S^{4+} to S^{6+} . In this series of reactions, SO_3 is an intermediate reaction product. The rate-limiting step, however, is the presence of the OH radical which is required to initiate the series of oxidation reactions (McKeen et al., 1984). The OH radical is produced by photolysis of ozone:



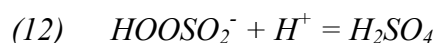
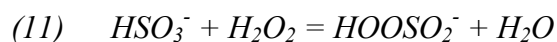
where $h\nu$ is a photon of solar radiation. If large amounts of SO_2 are injected into the stratosphere by a volcanic eruption, the SO_2 can absorb radiation that otherwise would be used to photolyze ozone, since both gases absorb at similar wavelengths. As a result, OH production may be reduced (McKeen et al., 1984; Pinto et al., 1989; Bekki, 1995). The net result would be a longer SO_2 lifetime in the stratosphere.

In general, these gas-phase reactions depend on the temperature and humidity of the surrounding environment. Low-temperature and low-humidity environments such as the stratosphere inhibit SO_2 conversion. Laj et al. (1990) estimate that the SO_2 conversion rate in the stratosphere is less than 1% per day. By contrast, high temperatures and humidities promote formation of the OH radical which reacts with SO_2 . However, the OH- SO_2 reaction will not be important until the volcanic gas plume has become sufficiently dilute to allow adequate mixing with the surrounding atmosphere. Eatough et al. (1994) has shown that SO_2 conversion rates are normally less than 15% SO_2 per hour, averaging about 5% per hour. These rates remain rather constant except under conditions of very high humidity.

2.3.2. Aqueous phase reactions

In cloud and fog, sulphur dioxide is dissolved into water droplets as HSO_3^- . The rate of dissolution is a function of both the size distribution and the chemistry of the droplets. Once dissolved, the sulphur is then oxidized from S^{4+} to S^{6+} . The oxidation rate depends on the type and amounts of oxidants which are present. At pH values higher than 5, ozone is an important oxidant. Typical atmospheric concentrations of ozone are 0.1-5 ppb. High pH values can be maintained by high levels of NH_3 .

Under low pH values which are more typical of a volcanic gas plume, H_2O_2 is an important oxidant for the following series of reactions:



It has been observed that SO_2 and H_2O_2 concentrations are frequently inversely correlated (Laj et al., 1990; 1997). The above reactions are rate-limited when SO_2 or H_2O_2 concentrations exceed 100 ppb (Schwartz and Freiberg, 1981). While this situation rarely arises for H_2O_2 , a concentrated SO_2 volcanic plume may have high SO_2 concentrations, which could both deplete H_2O_2 needed for oxidation and rate-limit the reactions. As a result, SO_2 lifetimes may be extended (Pinto et al., 1989). On the other hand, H_2O_2 is generated at the air-water interface (Zika et al., 1982), which could promote enhanced SO_2 oxidation for a volcanic plume passing over water. Ambient H_2O_2 concentrations are significantly higher during the summer months and at high latitudes (Eatough et al., 1994).

2.3.3. Heterogeneous reactions

These types of reactions are perhaps the least understood. The presence of volcanic ash in the gas plume probably plays an important and perhaps central role. The solid grains serve as nuclei onto which acid gases and aerosols are deposited (Rose, 1977). Particles grow larger by continued deposition and by coagulation (Pinto et al., 1989). Once the particles reach a certain size, they are removed from the gas plume by sedimentation. This process thus serves as a mechanism to remove SO_2 and other acid gases from the atmosphere. Evidence for this process of fractionation are the high concentrations of sulphur and chlorine in leachates of volcanic ash (Taylor and Stoiber, 1973; Rose, 1977).

At Mt. Etna, two studies have examined the rate of SO_2 depletion in the presence of ash. Jaeschke et al. (1982) measured rapid SO_2 conversion (k values of 10^{-4} to 10^{-3} s^{-1}), while Martin et al. (1986) observed significantly slower rates ($k = 10^{-6}$ to 10^{-5} s^{-1}). These differences may be the result of the different methods employed and/or different amounts of ash in the gas plume. Martin et al. (1986) suggested that the amount of SO_2 loss is a function of the amount and size distribution of particles that are present.

Oppenheimer et al. (1997) examined SO_2 depletion in the gas plume from the Soufrière Hills volcano, Montserrat. They observed significant SO_2 loss, which they attributed to the high levels of ash and aerosols in the gas column, the high ambient temperature and humidity, and the frequent presence of cloud and ash over the summit area. Oppenheimer et al. (1997) suggest that SO_2 loss and conversion are more rapid at low altitudes, suggesting an important effect of temperature and/or humidity.

3. ESTIMATES OF SULPHUR EMISSIONS FROM VOLCANOES TO THE ATMOSPHERE

Using a variety of techniques, different estimates of global subaerial volcanic SO_2 emissions have been made over the last 30 years. These estimates are compiled in Table 1. For this compilation, it is important to note that sulphur emissions from submarine volcanoes are not considered. For the estimates, three questions are of fundamental importance:

- the proportion of eruptive vs. non-eruptive SO_2 that is emitted;
- the proportion of tropospheric vs. stratospheric SO_2 ;
- the contribution of H_2S , SO_4^{2-} , and other trace sulphur species to the total volcanic sulphur budget.

Some general observations can be made from Table 1. (1) The majority of estimates arrive at a value of 10^{-20} Tg ($1\text{--}2 \times 10^7 \text{ tonnes}$) $\text{year}^{-1} \text{ SO}_2$. The estimates of Kellogg et al. (1972) and

Cadle (1975) are low (1.5 and 7.8 Tg year⁻¹ SO₂, respectively), probably because they considered degassing only from eruptive material and not from intrusive degassing. The estimates of Le Guern (1982) and Lambert et al. (1988) are high (50 Tg year⁻¹ SO₂). To calculate SO₂ emissions, Lambert et al. (1988) used an indirect technique by multiplying known quantities of ²¹⁰Po by SO₂/²¹⁰Po ratios of volcanic gas. It is possible that their ²¹⁰Po values and/or SO₂/²¹⁰Po ratios were too high, resulting in the elevated SO₂ estimates. (2) Estimates of the ratio of eruptive to non-eruptive SO₂ emissions range from 0.9 to 1.9, with the exception of one low value of 0.07 from Berresheim and Jaeschke (1983). As Stoiber et al. (1987) have noted, Berresheim and Jaeschke (1983) may have overestimated the number of non-erupting volcanoes that are actively degassing. (3) Berresheim and Jaeschke (1983) estimate volcanic H₂S emissions at 1 Tg year⁻¹ and SO₄²⁻ emissions at 10 Tg year⁻¹. Taylor and Stoiber (1973) calculate that 8 Tg year⁻¹ equivalent SO₂ are absorbed on ash from explosive eruptions; this is equivalent to 12 Tg year⁻¹ SO₄²⁻, which agrees with the estimate by Berresheim and Jaeschke (1983).

Table 1. Estimates of annual SO₂ emissions from subaerial volcanoes

Source	Eruptive	Non-eruptive	Eruptive / Non-eruptive	Troposphere	Stratosphere	Total
Kellogg et al. (1972)	1.5					1.5
Stoiber & Jepson (1973)						10 ^a
Cadle (1975)				7.5	0.28	7.6
Le Guern (1982)						50
Berresheim & Jaeschke (1983)	1.0	14	0.071			15 ^b
Stoiber et al. (1987)	12	6.8	1.8			19 ^c
Lambert et al. (1988)						50
Gerlach (1991)						13
Spiro et al. (1992)	10.2	5.4	1.9			16 ^d
Bluth et al. (1993)	6.1	6.8	0.90			13
Pyle et al. (1996)					0.4-1 ^e	
Chin et al. (1996)	8 ^g	5.4 ^h	1.5			13
Graf et al. (1997)	8	20	0.4	28		28 ⁱ

Notes:

All values in Tg (1 Tg = 1 Mt = 10⁶ tonnes). Emissions from submarine volcanoes not considered.

^a Ignores SO₂ produced during large explosive eruptions. ^b Period from 1961 to 1979. Volcanic H₂S: 1 Tg year⁻¹; volcanic 10 Tg year⁻¹; total volcanic sulphur: 12 Tg year⁻¹ (24 Tg year⁻¹ equivalent SO₂). ^c H₂S, SO₄²⁻ considered to be <10% of total volcanic sulphur emissions. ^d Average annual flux values for 1964-1972, expressed as equivalent SO₂; original data presented as elemental sulphur: eruptive 5.1 Tg year⁻¹ S, non-eruptive 2.7 Tg year⁻¹ S, total 7.8 Tg year⁻¹ S. ^e Short-term (10-20 years) flux 0.4 Tg year⁻¹, medium-term (10² years) SO₂ flux 1 Tg year⁻¹, long-term (10³ years) flux 0.5-1 Tg year⁻¹. ^f 1985: 29.6 Tg SO₂ 1990: 23.3 Tg SO₂. ^g Eruptive emissions for 1985. ^h Non-eruptive emissions from Spiro et al. (1992). ⁱ Average annual flux values, expressed as equivalent SO₂; original data presented as elemental sulphur. Stratospheric contributions ignored.

As a final point, several groups of workers have noted a positive correlation between the intensity of an explosive eruption at convergent margins volcanoes and the amount of SO₂ emitted by the eruption (Fig. 4) (Stoiber et al., 1987; Bluth et al., 1993; Pyle et al., 1996; Schnetzler et al., 1997). The correlation is good when the SO₂ data from various volcanoes are averaged for a particular VEI class (Fig. 4c). When individual volcanoes are plotted, however,

the correlation deteriorates (Fig. 4a, b). This observation indicates that explosivity is not the only parameter which determines how much SO_2 a volcano will release during eruption.

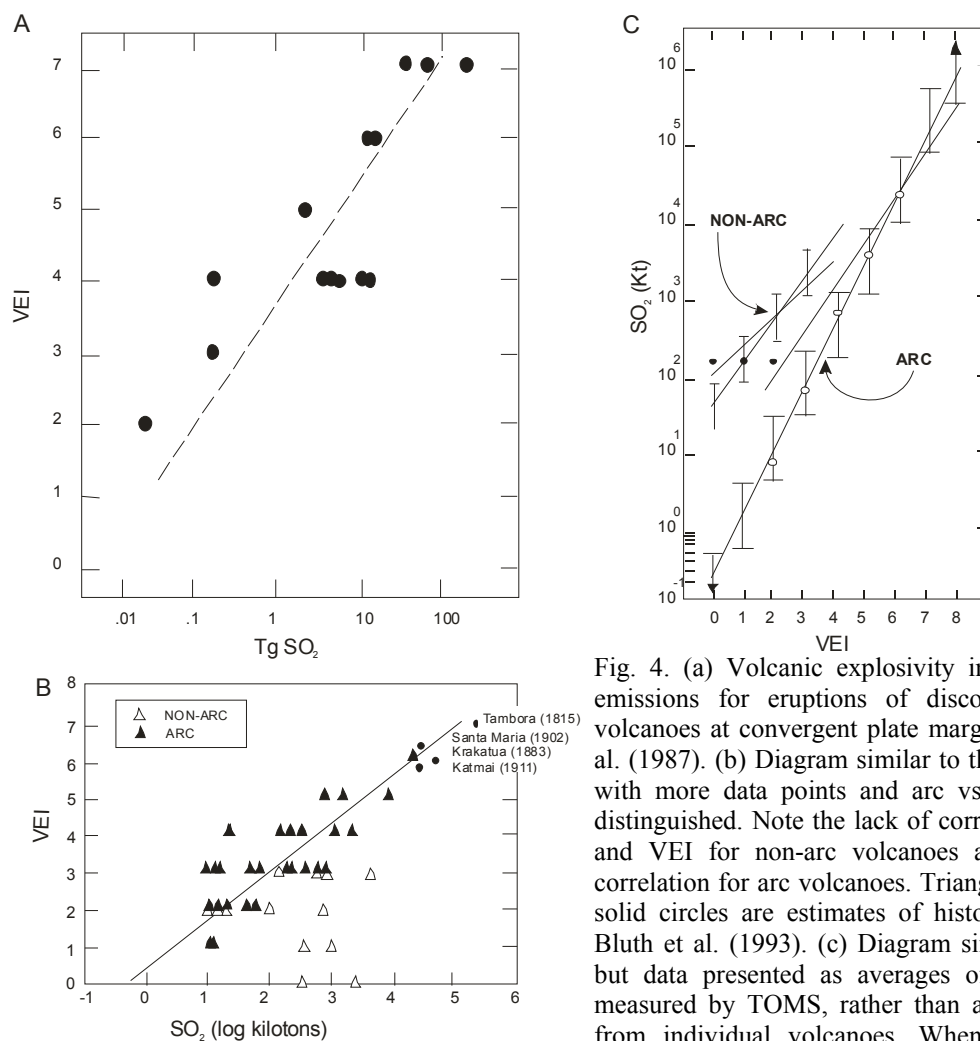


Fig. 4. (a) Volcanic explosivity index (VEI) vs. SO_2 emissions for eruptions of discontinuously erupting volcanoes at convergent plate margins. From Stoiber et al. (1987). (b) Diagram similar to that shown in (a), but with more data points and arc vs. non-arc volcanoes distinguished. Note the lack of correlation between SO_2 and VEI for non-arc volcanoes and the rather poor correlation for arc volcanoes. Triangles are TOMS data, solid circles are estimates of historic eruptions. From Bluth et al. (1993). (c) Diagram similar to (a) and (b), but data presented as averages of SO_2 emissions as measured by TOMS, rather than as single data points from individual volcanoes. When the SO_2 data are averaged, the apparent correlation between SO_2 and VEI for arc volcanoes appears to improve. Dashed lines are from Stoiber et al. (1987). Figure from Schnetzler et al. (1997).

4. CASE STUDIES OF COSPEC MEASUREMENTS AT VOLCANOES

While SO_2 fluxes have been measured from many volcanoes, the fluxes generally are not measured on a regular basis. Only a very few volcanoes are monitored intensively with the COSPEC, yet these data are the most useful for helping understand how a volcano works. Fortunately, this situation is changing as more volcano observatories acquire COSPECs and begin to collect data systematically.

In this section we summarize and synthesize COSPEC results from several well-studied volcanoes. This summary is not meant to be comprehensive, but rather to highlight interesting results that have been obtained with the COSPEC at different volcanoes. We begin by examining five volcanoes which are either basaltic (Kīlauea, Mt. Etna, Masaya, Arenal) or phonolitic (Mt. Erebus) and whose conduit systems generally remain open to degassing. We then look at several andesitic volcanoes which tend to degas in a more discontinuous, closed fashion (Mt. St. Helens, Mt. Pinatubo, Galeras, Redoubt). This second group also erupts more explosively and discontinuously than the first group.

4.1. Kīlauea (Hawaii, USA)

Kīlauea volcano currently erupts from both the summit crater of Halemaumau and along the East Rift Zone. COSPEC work at Kīlauea has focused on degassing at the summit crater of Halema'uma'u (Casadevall et al., 1987; Connor et al., 1988) and along the East Rift Zone (Casadevall et al., 1987; Chartier et al., 1988; Andres et al., 1989). Connor et al. (1988) analyzed a set of data that were collected in 1979 at Halema'uma'u by means of a vehicle-mounted COSPEC. They used a moving statistics approach to remove short-term noise in order to recognize longer frequency variations in the SO_2 emissions (Fig. 5a). This approach is a means to reduce daily variations which are often inherent in COSPEC data. The filtered SO_2 data are shown in Figure 5b, along with tidal oscillations and volcanic earthquakes.

There is an apparent positive correlation between SO_2 and 14-day solid earth tides, as well as possibly higher SO_2 levels during increased short-period earthquake activity. Such a statistical approach can be used to filter noisy data, which pose a problem for interpretation. On the other hand, filtering techniques necessitate a large number of data points, and one must take care not to filter the data excessively, as this could obscure interesting short-term variations.

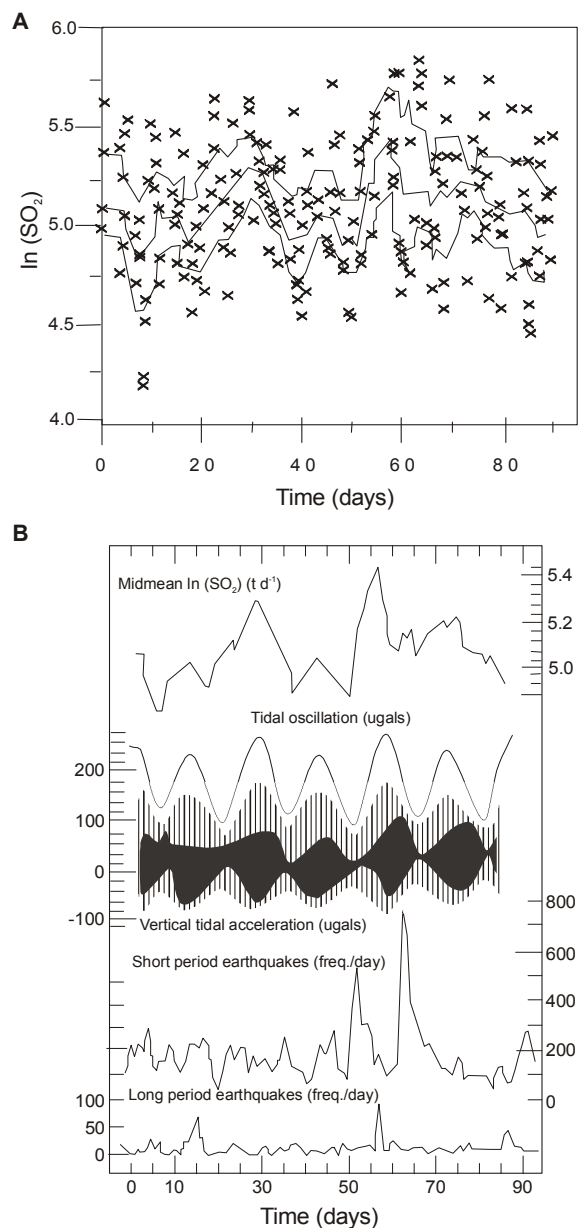


Fig. 5. SO_2 flux (t d^{-1}) vs. time at Halema'uma'u crater, Kīlauea caldera, Hawaii. Day 0 is 10 June 1979. Moving statistics: upper line is upper semimidmean, middle line is midmean, lower line is lower semimidmean. (b) Midmean of SO_2 flux compared to tidal fluctuations and seismicity for Halemaumau. Day 0 is 10 June 1979. From Connor et al. (1988).

Chartier et al. (1988) used stationary techniques to measure SO_2 fluxes from the Pu'u 'Ō'ō vent between 13 June and 6 July 1985 during Episode 33 of the East Rift Zone eruption. The purpose of the study was to measure SO_2 flux variations from mainly quiescent degassing between fire fountaining episodes at Pu'u 'Ō'ō. The average flux was $170 \pm 80 \text{ t d}^{-1}$, and the data are suggestive of a decline in fluxes with time (Fig. 6a), although there are some short-term excursions observed. Brief periods of fountaining were correlated with increases in SO_2 emissions on a timescale of hours; on 12 June 1985, SO_2 fluxes increased from 150–450 t d^{-1} before fountaining to 400–600 t d^{-1} during fountaining (Fig. 6b). These observations suggest the magma was more gas-rich at high levels, and/or more convective, promoting enhanced vesiculation. During Episode 24, “puffing” could be observed; for example, on 24 August 1984, SO_2 fluxes varied from essentially zero to nearly 600 t d^{-1} over the space of minutes (Fig. 6c). Such variations were attributed to convection, bubble nucleation and coalescence, variable magma supply rates, and/or repeated opening and closing of the conduit (Chartier et al., 1988; Andres et al., 1989).

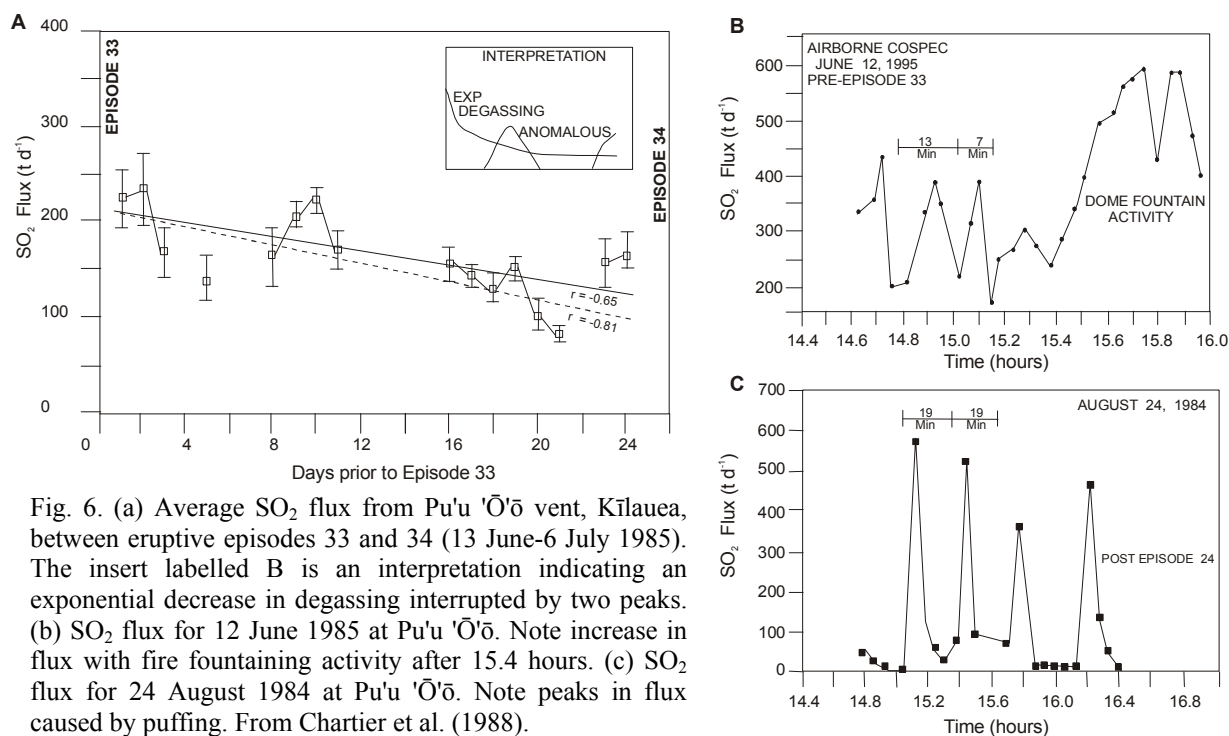


Fig. 6. (a) Average SO_2 flux from Pu'u 'Ō'ō vent, Kīlauea, between eruptive episodes 33 and 34 (13 June–6 July 1985). The insert labelled B is an interpretation indicating an exponential decrease in degassing interrupted by two peaks. (b) SO_2 flux for 12 June 1985 at Pu'u 'Ō'ō. Note increase in flux with fire fountaining activity after 15.4 hours. (c) SO_2 flux for 24 August 1984 at Pu'u 'Ō'ō. Note peaks in flux caused by puffing. From Chartier et al. (1988).

By July 1986 the episodes of fountaining from Pu'u 'Ō'ō were replaced by continuous extrusion from the Kupaianahu vent, which is located about 3 km east-northeast of Pu'u 'Ō'ō. COSPEC measurements were made by Andres et al. (1989) using mobile techniques in a car along the Chain of Craters road. The average SO_2 flux of $1170 \pm 400 \text{ t d}^{-1}$ was much less than the 5,100–32,000 t d^{-1} of the 1983–1985 high fountaining episodes from Pu'u 'Ō'ō (Casadevall et al., 1987), but higher than either contemporaneous fluxes from Halema'uma'u or interphase Pu'u 'Ō'ō emissions (e.g., Chartier et al., 1988). Andres et al. (1989) estimated that Pu'u 'Ō'ō contributed two thirds of the SO_2 and Kupaianaha the other third. Using infrared TIMS images from September 1988, Realmuto et al. (1997) found that these contributions from the two vents were unchanged from 1986. They also were able to map spatial variations in SO_2 concentrations which were the result of puffing.

4.2. Mt. Etna (Italy)

A large body of SO₂ data has been collected at Mt. Etna. The first measurements were made in the late 1970's by several groups who showed that Mt. Etna releases large amounts of SO₂ and other gases (Haulet et al., 1977; Malinconico, 1979).

During a period of intermittent summit activity in July-August 1977, Malinconico (1979) measured SO₂ fluxes by an upward-looking COSPEC in a vehicle. He showed increases in SO₂ 2-5 days before summit ash eruptions and fire fountaining. SO₂ fluxes rose from about 1,000 t d⁻¹ beforehand to 5,000-6,000 t d⁻¹ during the eruptions (Fig. 7). The SO₂ fluxes declined rapidly once the eruptions ended. A more gradual increase in SO₂ also was measured over ten days prior to a brief period of lava extrusion (Fig. 7). Malinconico (1979) suggested that the SO₂ fluxes correlate positively with the level of magma in the central conduit. These variations in SO₂ flux may help forecast eruptions.

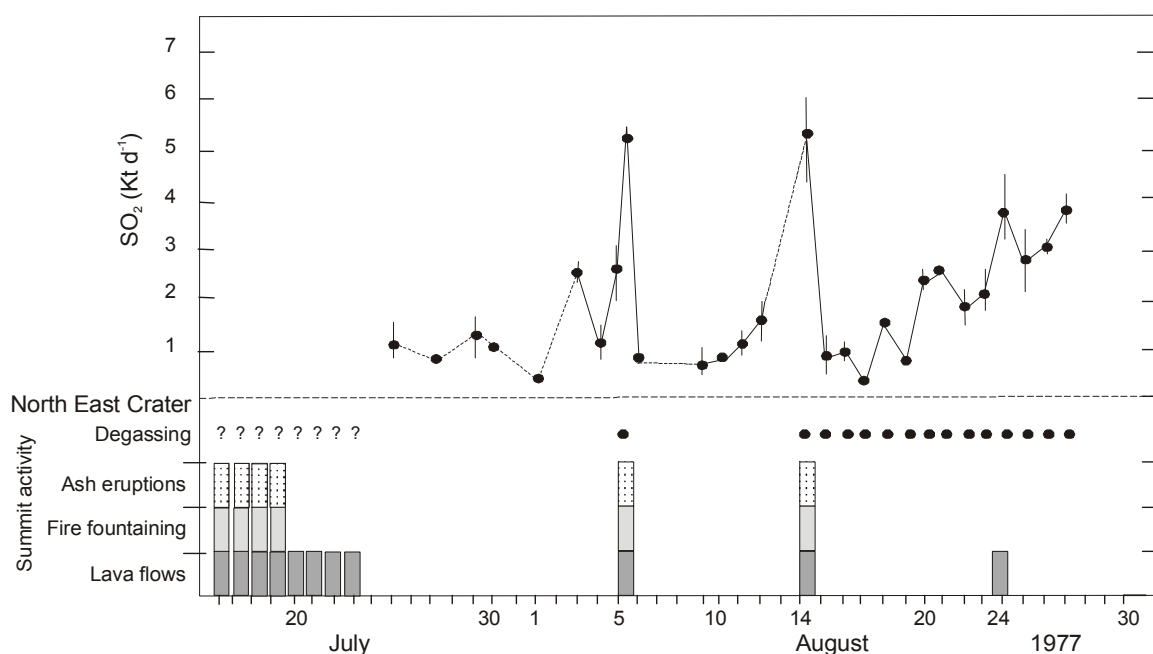


Fig. 7. SO₂ fluxes from Mt. Etna, Italy, July-August 1977. Also shown are periods of summit degassing, ash eruptions, fire fountaining, and lava flows. The two large SO₂ peaks are correlated with increased summit activity. From Malinconico (1979).

Since 1987, workers have employed vehicle-based mobile techniques, mainly on roads east of the summit area, to measure the SO₂ fluxes on a regular basis (Caltabiano et al., 1994; Bruno et al., 1994). The results of these systematic studies are interesting, since they shed light on changes in SO₂ emissions as a function of eruptive activity over a seven-year period. Caltabiano et al. (1994) make four major observations:

- Quiet summit degassing averages 5,500 t d⁻¹.
- Brief eruptive periods in 1989 and 1990 were characterized by high fluxes reaching 10,000-25,000 t d⁻¹.
- Fluxes appeared to reach a minimum level about one month before important eruptive events, as a result of conduit sealing or a drop in magma level as deeper fractures developed.

- When the conduit was open, both the level of the magma and the amount of tremor were positively correlated with SO₂ fluxes (e.g., Fig. 8). Higher magma levels and increased tremor are probably the result of increased vesiculation and degassing.

The 1991-1993 activity at Mt. Etna consisted of a flank eruption along the southeast fissure which began on 14 December 1991. The eruption was accompanied by continual degassing from the summit area. Low SO₂ fluxes were noted for several months prior to the onset of the eruption, with a minimum of 840 t d⁻¹ recorded on 8 November 1991 (Bruno et al., 1994; Caltabiano et al., 1994). The trend of SO₂ emissions during the 1991-1993 eruption was divided into four intervals (I, II, III, IV) by Bruno et al. (1994). Interval I was characterized by high SO₂ levels, on occasion exceeding 15,000 t d⁻¹. Interval II showed an overall decline, with maximum values less than 5,000 t d⁻¹. Intervals III and IV showed increases, with highest values reaching 10,000-15,000 t d⁻¹ (Fig. 9a). The SO₂ fluxes exhibited good positive correlations with tilt, with declines in both SO₂ flux and tilt observed during Intervals I and II followed by increases during III and IV (Fig. 9). Bruno et al. (1994) interpreted these changes as the degassing and emptying of magma through the southeast fissure during Intervals I and II, with recharge of new magma occurring during Intervals III and IV, causing inflation and renewed degassing.

Fig. 8. (a) SO₂ fluxes at Mt. Etna, 1987-1991. Cumulative fluxes also are shown on the right vertical axis and are plotted as a curve with positive slope. (b) Volcanic tremor at Mt. Etna for the same period as in (a). Cumulative tremor also is shown on the right vertical axis and is plotted as a curve with positive slope. From Caltabiano et al. (1994).

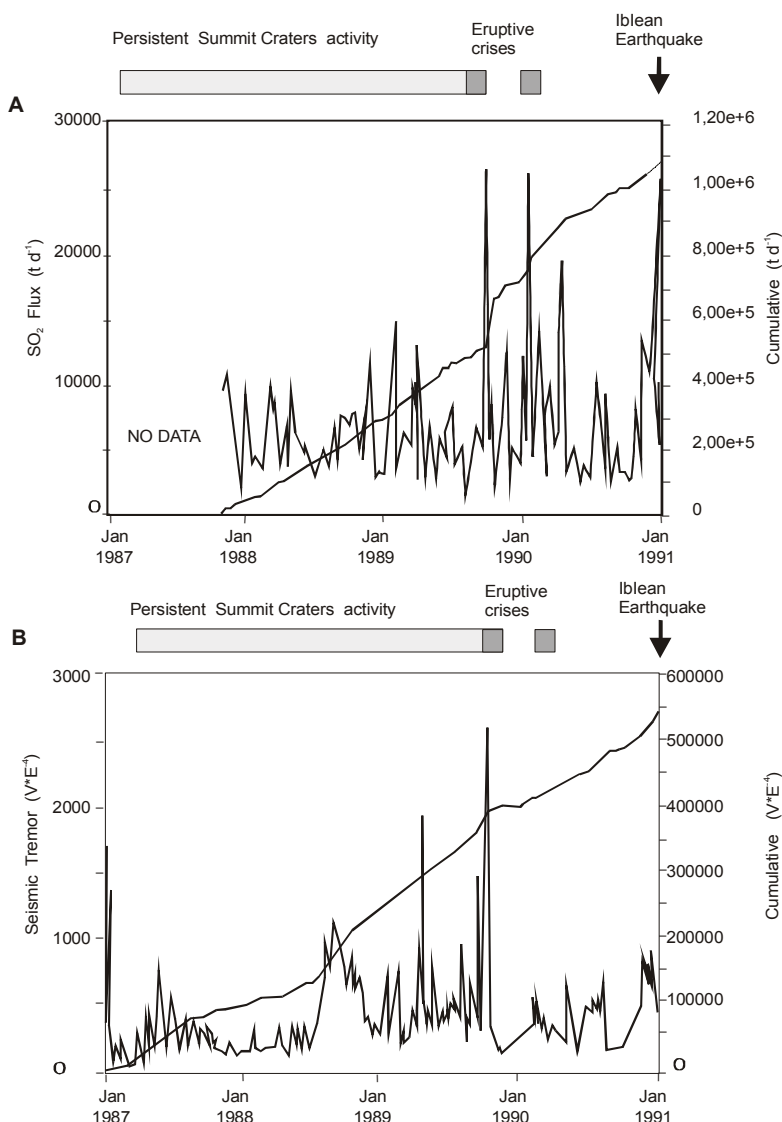
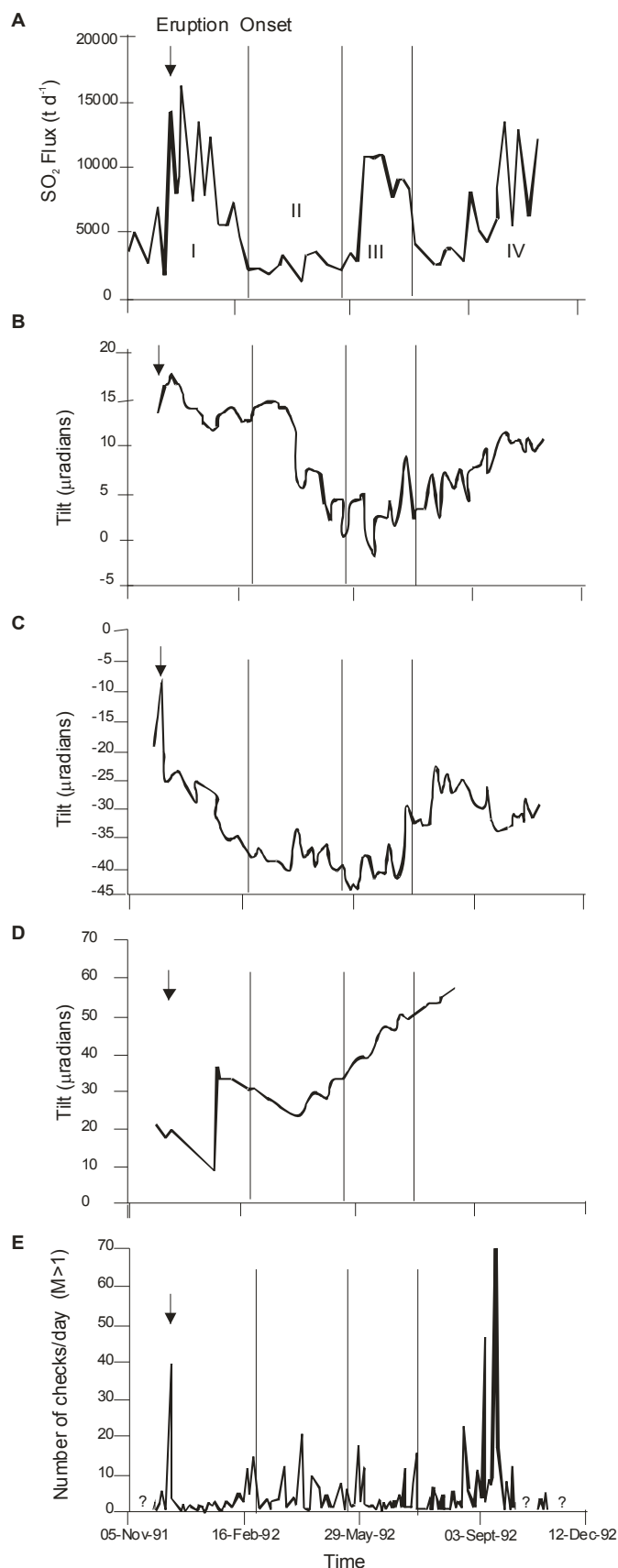


Fig. 9. (a) SO_2 fluxes at Mt. Etna, 1991-1992. Vertical arrow indicates the beginning of the 1991-1993 southeast flank eruption. (b) Radial tilt recorded at the SPC station during the same time period. (c) Tangential tilt at the SPC station during the same period. (d) Radial tilt at the CDV station during the same period. (e) Volcanic earthquakes at Mt. Etna recorded during the same time period. From Bruno et al. (1994).



4.3. Masaya (Nicaragua)

Masaya is known for repeated episodes of strong degassing which adversely affect the surrounding region. These episodes last for years to tens of years. COSPEC measurements are made from a vehicle which is driven beneath the plume to the west of the active Santiago crater. This is the only effective way to make measurements, as the gas plume often hugs the ground, particularly along the Llano Pacaya which is located west of the volcano at higher elevations than the crater.

Stoiber et al. (1986) and Delmelle et al. (1999) have mapped the area which is affected by the gases from Masaya (Fig. 10). As a result of easterly trade winds, a broad region to the west of the volcano suffers from the effects of acid gases, including SO_2 . For example, pH values of 2.6 were recorded in rain falling several kilometers west of the volcano on 18-19 August 1980 (Johnson and Parnell, 1986).

Stoiber et al. (1986) measured an increase in SO_2 emissions from 380 t d^{-1} in the late 1970's to about $1,200 \text{ t d}^{-1}$ in February 1980. They also noted possible correlations between SO_2 emissions and the solid earth tide over the course of a day (Fig. 11). For 7 January 1982, SO_2 maximums appear to occur near the tidal minimum, while the reverse is true for 8 January. By contrast, no particular trend is evident for 9 January. Large bursts of gas ($>1,500 \text{ t d}^{-1}$) on 7 and 9 January appeared to occur at times of maximum inflection on the tidal curves (Fig. 11).

Volcanoes such as Masaya and Halemaumau have open plumbing systems; for example, both have had periods of lava lake activity. The open nature of these systems suggests that they may be sensitive to tidal influences. The work by Stoiber et al. (1986) and Connor et al. (1988) are good starting points from which to pursue this avenue of research.

Rymer et al. (1998) and Williams-Jones et al. (2003) studied correlations between micro-gravity and SO_2 fluxes during a degassing crisis which began in 1993. In 1996 the average SO_2 flux was $600 \pm 290 \text{ t d}^{-1}$, while by 1997 the average flux had decreased to $400 \pm 200 \text{ t d}^{-1}$. This was followed by a sharp increase in 1998 to $1870 \pm 960 \text{ t d}^{-1}$. Subsequently, gas flux decreased progressively to $550 \pm 250 \text{ t d}^{-1}$ in 2001. Beginning in 1993, gravity decreases in the summit area signalled a loss of mass from the magmatic system. Interestingly, the mass loss calculated from the gravity data was the same as that calculated from the COSPEC data (2.6×10^6 tonnes). Thus, the loss in mass likely was the result of progressive degassing, beginning with the reactivation in 1993. Continued variations in gravity led Rymer et al. (1998) and Williams-Jones et al. (2003) hypothesize that the initiation of degassing in 1993 was caused by convective overturn, bringing low-density, gas-rich magma to shallow levels. Furthermore, the inverse relationship between gravity change and gas flux suggests that this type of process is cyclical in nature. This example

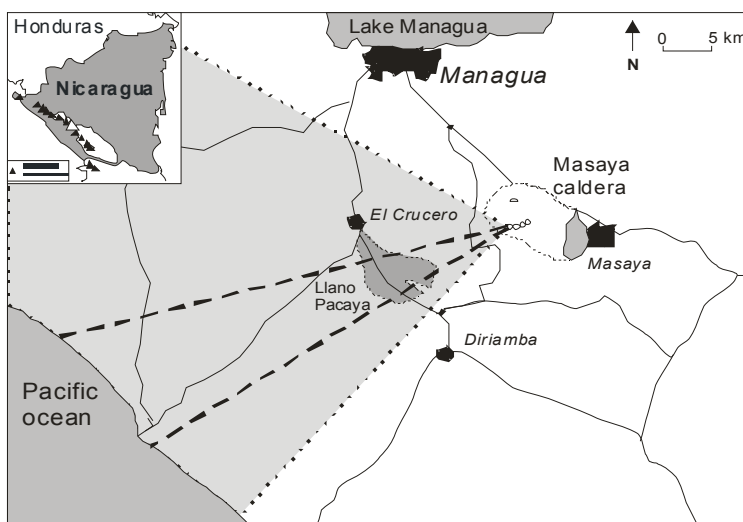


Fig. 10. Dispersion of gas from Masaya volcano, Nicaragua. The thick dashed lines indicate the area affected by a typical plume, while the shaded area indicates the full extent of plume gas effects on the region.

shows the benefits of integrating the COSPEC data with other geophysical parameters such as micro-gravity.

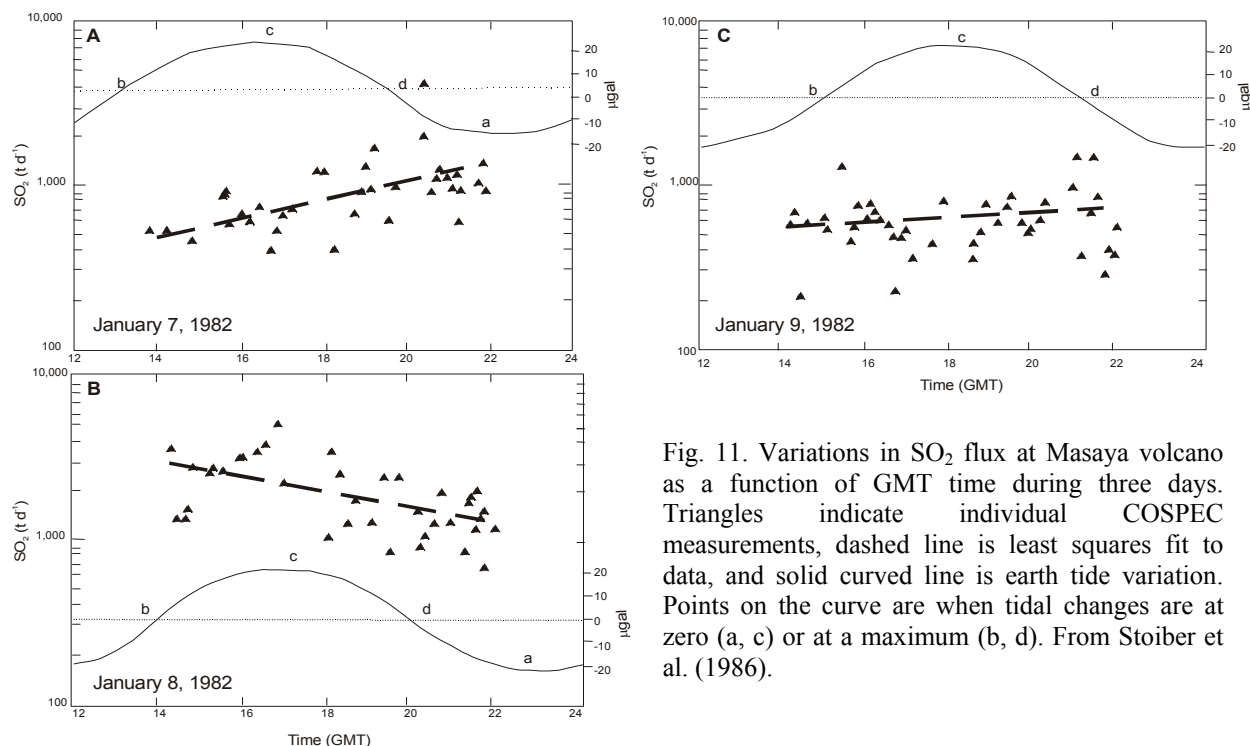


Fig. 11. Variations in SO_2 flux at Masaya volcano as a function of GMT time during three days. Triangles indicate individual COSPEC measurements, dashed line is least squares fit to data, and solid curved line is earth tide variation. Points on the curve are when tidal changes are at zero (a, c) or at a maximum (b, d). From Stoiber et al. (1986).

4.4. Arenal (Costa Rica)

Arenal volcano has been almost continuously in eruption since its reactivation in July 1968. Gas emissions from the volcano have been both by passive degassing and explosive eruptions, with passive degassing being dominant. COSPEC measurements were first made at Arenal in 1982 using stationary and airborne techniques which had average SO_2 fluxes of $\sim 50 \text{ t d}^{-1}$ and $198 \pm 40 \text{ t d}^{-1}$, respectively (Stoiber et al., 1982; Casadevall et al., 1984).

In 1995 and 1996, Williams-Jones et al. (2001) made over 150 vehicle-based COSPEC measurements along a road bordering the western flank of the volcano, resulting in an average SO_2 flux of $128 \pm 60 \text{ t d}^{-1}$. Due to the high level and frequency of eruptive activity at Arenal, it was difficult to obtain the statistical data necessary to prove systematic decreases in SO_2 levels prior to an eruption. There are, however, some instances where SO_2 levels appear to decrease progressively prior to an explosive eruption. For example, on 8 March 1996, SO_2 was seen to drop from $360 \pm 50 \text{ t d}^{-1}$ (likely from an unrecorded eruption) to $110 \pm 20 \text{ t d}^{-1}$ before an eruption at 1219 hours, and subsequently climbed to $242 \pm 36 \text{ t d}^{-1}$ immediately afterwards (Fig. 12a).

SO_2 flux and tremor fluctuations also showed a distinct correlation with Earth tides; decreased explosive activity and increased tremor coincide with the peak of high tide. The amplitudes of the morning eruptions tend to be greater and more variable than those of the afternoon. The subsequent decrease in afternoon eruption occurrences and amplitudes generally coincided with the peak in predicted Earth tide gravity values. For example, prior to ~ 1326 hrs on March 5, there was very little chugging (locomotive-like sounds believed to be caused by repetitive gas emissions) or tremor activity; however, after this point significant tremor

commenced and lasted throughout the afternoon until the cessation of measurements at ~1600 hrs (Fig. 12b, c).

Arenal is likely tapping a deep to mid-crustal magma chamber and, unlike many volcanoes (e.g., Mount Pinatubo, Lascar), there is little difference between petrological and COSPEC SO_2 estimates (0.61 Mt vs 1.3 Mt, respectively), suggesting that Arenal is being continuously supplied by fresh magma. However, the open system is periodically blocked near the surface due to crystallisation of magma in the conduit and/or variations in extrusion rate. This results in the development of a temporary seal, leading to the overpressurisation of the conduit and eventual explosive destruction of the seal (Williams-Jones et al., 2001). Arenal's high level of activity allows for the study of multiple cycles of conduit opening and closing and thus is useful for better understanding the manner in which an open-system volcano degasses.

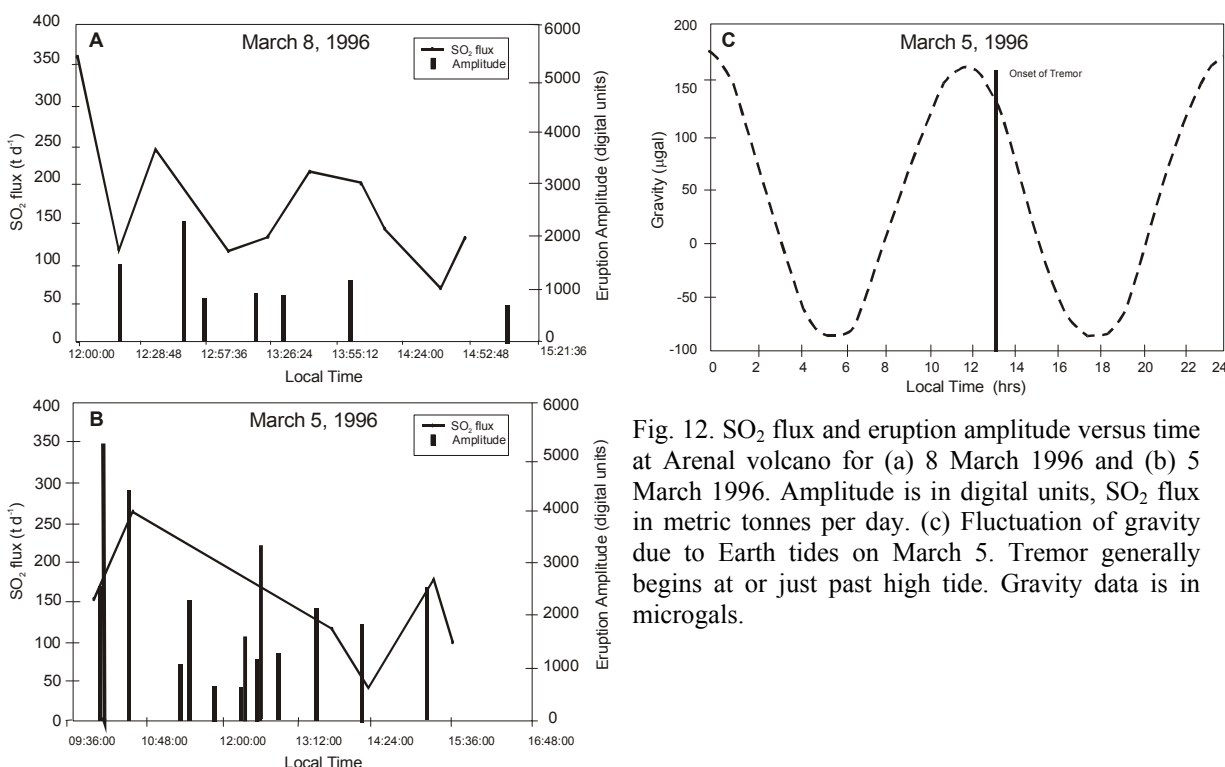


Fig. 12. SO_2 flux and eruption amplitude versus time at Arenal volcano for (a) 8 March 1996 and (b) 5 March 1996. Amplitude is in digital units, SO_2 flux in metric tonnes per day. (c) Fluctuation of gravity due to Earth tides on March 5. Tremor generally begins at or just past high tide. Gravity data is in microgals.

4.5. Mt. Erebus (Antarctica)

Mt. Erebus is the only known terrestrial example of a phonolitic lava lake. Therefore, it should show certain similarities with volcanoes such as Kīlauea and Masaya. COSPEC measurements were made initially in 1983 by aircraft (Rose et al., 1985) and subsequently by stationary techniques (Kyle et al., 1994). SO_2 fluxes are generally low ($<100 \text{ t d}^{-1}$), except for 1983 ($230 \pm 90 \text{ t d}^{-1}$) (Rose et al., 1985; Kyle et al., 1994). The average SO_2

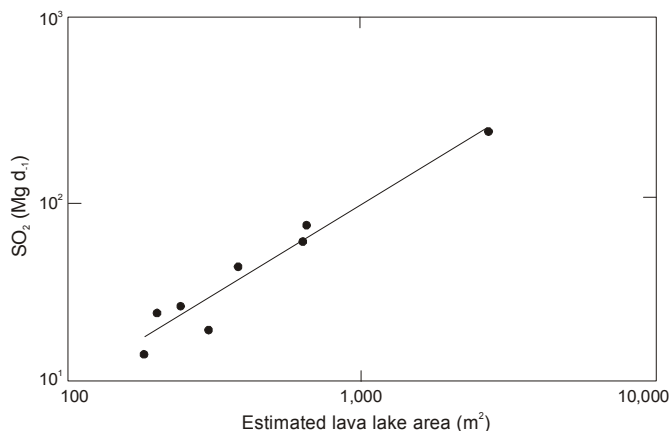


Fig. 13. SO_2 flux vs. lava lake area, Mt. Erebus, Antarctica. From Kyle et al. (1994).

emissions correlate positively with the surface area of the lava lake (Fig. 13), implying that SO_2 is released at shallow levels (Kyle et al., 1994). Daily variations of SO_2 may be the result of convection (Kyle et al., 1994), although earth tides also could play a role.

4.6. Mt. St. Helens (Washington, USA)

Mt. St. Helens is an interesting case history, since SO_2 fluxes were measured by COSPEC both before (Stoiber et al., 1980; Casadevall et al., 1981) and after the paroxysmal 18 May 1980 eruption (Stoiber et al., 1981; Casadevall et al., 1981; 1983). In addition, TOMS satellite SO_2 measurements were made of the 18 May stratospheric plume (Bluth et al., 1993), and distal COSPEC measurements were made of the 18 May gas plume as it passed over Toronto, Canada, several days later (Millán et al., 1985). As a result, a model of degassing can be constructed for the volcano. This is of great benefit in attempting to understand the behavior of a volcano, and it only can be done when SO_2 (and other) data are collected at points which are closely spaced in time. Before 18 May, COSPEC SO_2 flux measurements were made by aircraft, helicopter, and stationary ground techniques (Stoiber et al., 1980; 1981; Casadevall et al., 1981). SO_2 emissions were very low ($<50 \text{ t d}^{-1}$) for approximately seven

weeks preceding the 18 May eruption. Considering the large magnitude of the 18 May eruption, this is an interesting result, which may be the result of several factors (Casadevall et al., 1981):

- the majority of the magma being at deep levels ($> 7 \text{ km}$) (Pallister et al., 1992), hindering exsolution of SO_2 ;
- sealing of the cryptodome;
- high levels of H_2S in low-temperature gases (Hobbs et al., 1981; 1982), the low temperatures hindering oxidation to SO_2 ;
- absorption of SO_2 into the hydrothermal system.

This is an excellent example of very low SO_2 emissions preceding large explosive eruptions. The low S/Cl ratios measured for ash leachates during this period also are consistent with the low SO_2 fluxes; the combined data indicate that the magmatic gas component was small before 18

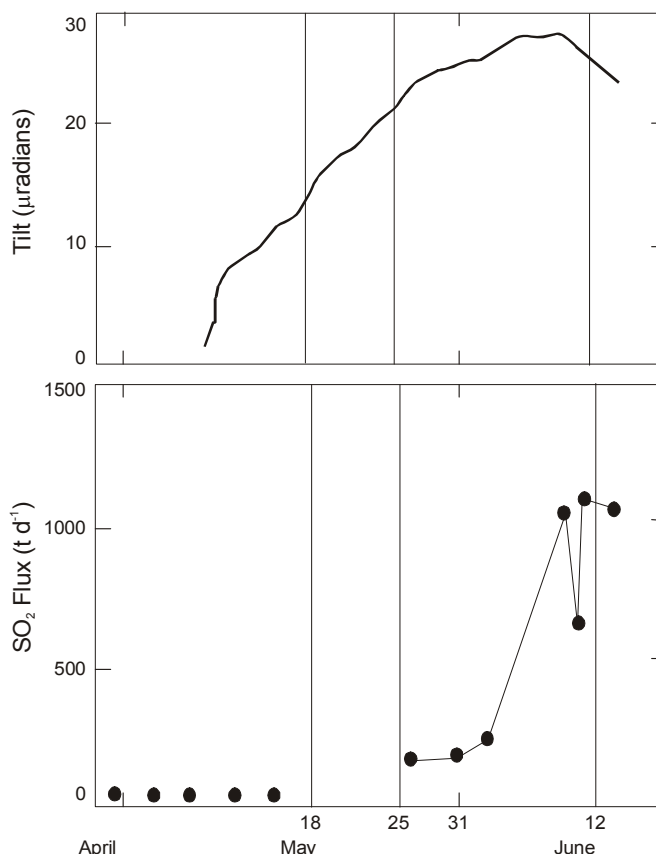


Fig. 14. SO_2 fluxes from Mt. St. Helens, Washington, April-June 1980. Also shown are changes in tilt at the Ape Cave North station, located 6 km southwest of the summit. The three vertical lines passing through the graphs indicate eruptions on 18 May, 25 May, and 12 June. From Casadevall et al. (1981).

May (Stoiber et al., 1980; 1981). Low levels of SO₂ before explosive eruptions also have been noted at Mt. Pinatubo, Galeras, and Redoubt volcanoes (see below).

The 18 May 1980 eruption released $0.24\text{--}1.1 \times 10^6$ tonnes of sulphur (0.24–1.1 Tg), equivalent to $0.48\text{--}2.2 \times 10^6$ tonnes SO₂ (0.48–2.2 Tg) (Stoiber et al., 1981; Millán et al., 1985; Bluth et al., 1993). There is some controversy regarding the proportions of SO₂ and H₂S which were injected into the atmosphere. Hobbs et al. (1981, 1982) contend that up to 90% of the sulphur was released as H₂S. By contrast, Turco et al. (1983) suggested either that the H₂S was rapidly oxidized to SO₂, or that the dominant sulphur species was in fact SO₂, not H₂S. Millán et al. (1985) made a stationary COSPEC measurement of the distal gas plume as it passed over Toronto 2–3 days after the 18 May eruption. Making some assumptions about plume width and height and SO₂–SO₄²⁻ conversion rates, they estimated 2.14×10^6 tonnes SO₂ (2.14 Tg) were released by the 18 May eruption. They made the important point that not only was SO₂ converted to SO₄²⁻ in the atmosphere, an unknown amount of H₂S was oxidized and converted to SO₂. This value is about twice that calculated using TOMS satellite data (1.0 ± 0.3 Tg SO₂) (Bluth et al., 1993; Gerlach and McGee, 1994).

SO₂ from eruptive degassing on 25 May was measured by COSPEC at $2,500 \text{ t d}^{-1}$, while passive degassing of SO₂ between eruptions remained low ($130\text{--}260 \text{ t d}^{-1}$) between 25 May and 3 June 1980 (Casadevall et al., 1981; Stoiber et al., 1981). The low SO₂ fluxes during this time are consistent with high H₂S/SO₂ ratios of 15 on 25 May and 6.8 on 30 May (Hobbs et al., 1981). By contrast, Stoiber et al. (1981) measured high S/Cl in ash leachates from the 18 May eruption, which were indicative of a large magmatic gas component. Then on 6 June, COSPEC SO₂ values increased to near $1,000 \text{ t d}^{-1}$ at the end of a period of inflation (Fig. 14), followed by an explosive eruption on 12 June and the first observation of a lava dome on 15 June. H₂S/SO₂ ratios in the plume declined to 0.87 on 4 June and 0.36 on 13 June (Hobbs et al., 1981; 1982). These changes are interpreted by Casadevall et al. (1981) as due to the rise of magma in a more open conduit, causing decompressive degassing and an increase in SO₂ emissions. Interestingly, the SO₂ increase occurred near or at the end of the inflation (Fig. 14), implying that SO₂ was released at shallow levels (Stoiber et al., 1981). During this period, SO₂ was released mainly by passive degassing, in contrast to before 6 June when explosive eruptions released the majority of the SO₂.

During 1980–1982, the volcano was characterized by repeated dome growth and destruction. During this time there was a steady overall decline in SO₂ emissions as measured by COSPEC (Fig. 15a). This trend was interpreted as the progressive degassing of a single batch of magma (Casadevall et al., 1983). This interpretation is consistent with changes in fumarolic gases during 1980–1981, whose compositions were progressively depleted in CO₂ and enriched in H₂O (Fig. 15b) (Casadevall et al., 1983).

4.7. *Mt. Pinatubo (Philippines)*

Mt. Pinatubo is a volcano located in the Luzon volcanic arc. The volcano reactivated in March 1991 when nearby residents began feeling earthquakes. Steam explosions occurred on 2 April 1991, and the climactic explosive eruptions occurred 10 weeks later on 15 June. COSPEC measurements by helicopter and airplane were begun on 13 May 1991, approximately one month before the climactic eruption. Initial values of 500 t d^{-1} indicated the presence of magma beneath the volcano; this evidence preceded seismic evidence of magma by about two weeks (Fig. 16) (Daag et al., 1996). SO₂ fluxes increased to $5,000 \text{ t d}^{-1}$ by the end of May, clearly indicative of

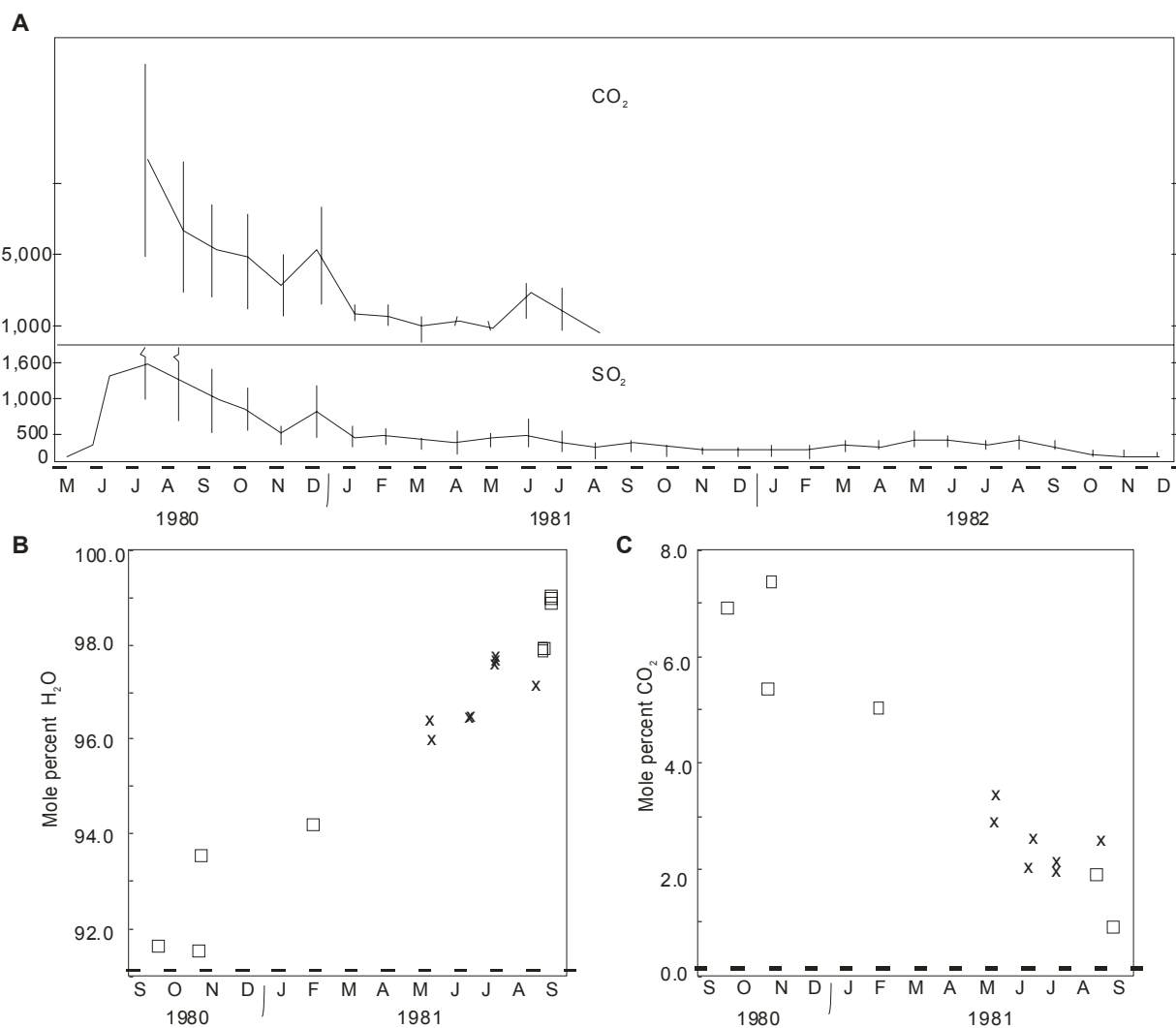


Fig. 15. (a) Average SO₂ and CO₂ fluxes in metric tonnes per day from Mt. St. Helens, 1980-1982. Note progressive declines in fluxes with time. (b) H₂O and CO₂ concentrations in gas from crater fumaroles, Mt. St. Helens, 1980-1981. Open squares represent complete gas analyses, X's represent noncondensable gas analyses. From Casadevall et al. (1983).

magma that was rising and/or actively degassing. The SO₂ fluxes then declined progressively to a minimum value of 260 t d⁻¹ on 5 June, suggesting that the magmatic system was sealing itself possibly pressurizing (Daag et al., 1996). Massive increases to >13,500 t d⁻¹ on 10 June signalled that a major eruption was imminent (Fig. 16) (Daag et al., 1996).

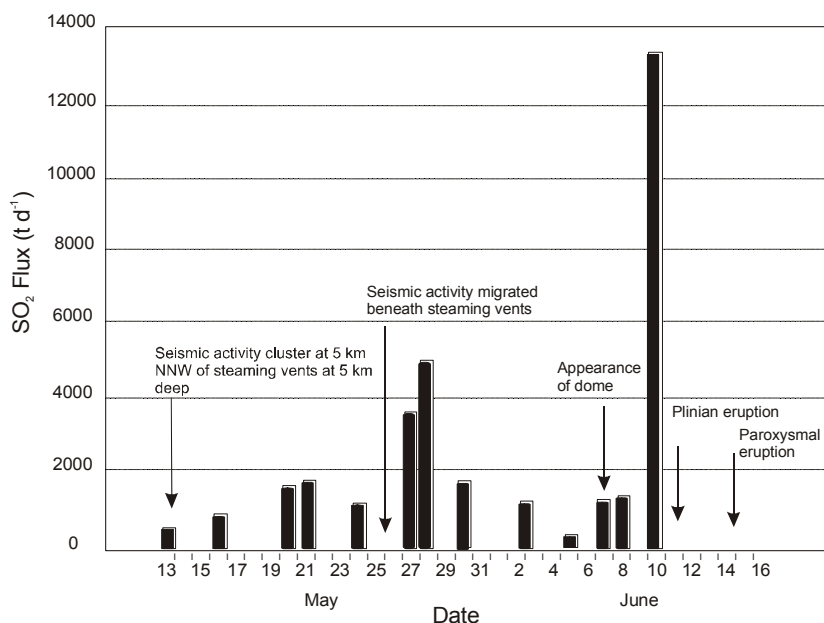


Fig. 16. SO₂ fluxes from Mt. Pinatubo, Philippines, May-June 1991. Note the very low value on 5 May and very high value on 10 May. From Daag et al. (1996).

4.8. Galeras (Colombia)

Galeras is the most active volcano in Colombia. COSPEC measurements at Galeras have been made by vehicle on a ring road encircling the volcano. Galeras reactivated in 1988, and showed high levels of degassing during 1989-1990, at times exceeding 5,000 t d⁻¹ (Fig. 17). A decline was noted in 1991, particularly after a lava dome was emplaced in the active crater in October-November 1991. The lower SO₂ levels were the result of both progressive degassing and conduit obstruction by the plug of magma that had formed the dome (Stix et al., 1993; Zapata et al., 1997). After the dome was emplaced, magma ceased to rise; thus, degassing changed from decompressive to static.

Correlations between SO₂ fluxes and long-period seismicity were observed on two timescales. After dome emplacement in October-November 1991, SO₂ fluxes were low, while long-period seismic events were still common (Fig. 17). In mid-July 1992, the number of long-period seismic events declined from >30/day to <30/day (Stix et al., 1997). This change occurred immediately before the dome was destroyed by an explosive eruption on 16 July 1992 (Cortés and Raigosa, 1997). Occasionally high SO₂ fluxes (>1,000 t d⁻¹) were measured in the weeks preceding the eruption, while low values (<500 t d⁻¹) were observed afterward (Zapata et al., 1997). One interpretation of these gas and seismic data is that the volcano's shallow plumbing system changed in July 1992 from a comparatively open vent to one that was partially closed. This is consistent with the five explosive eruptions recorded in the first half of 1993, which were caused by gas entrapment and build up beneath the volcano (Fischer et al., 1994; Cortés and Raigosa, 1997; Narváez et al., 1997; Gómez and Torres, 1997).

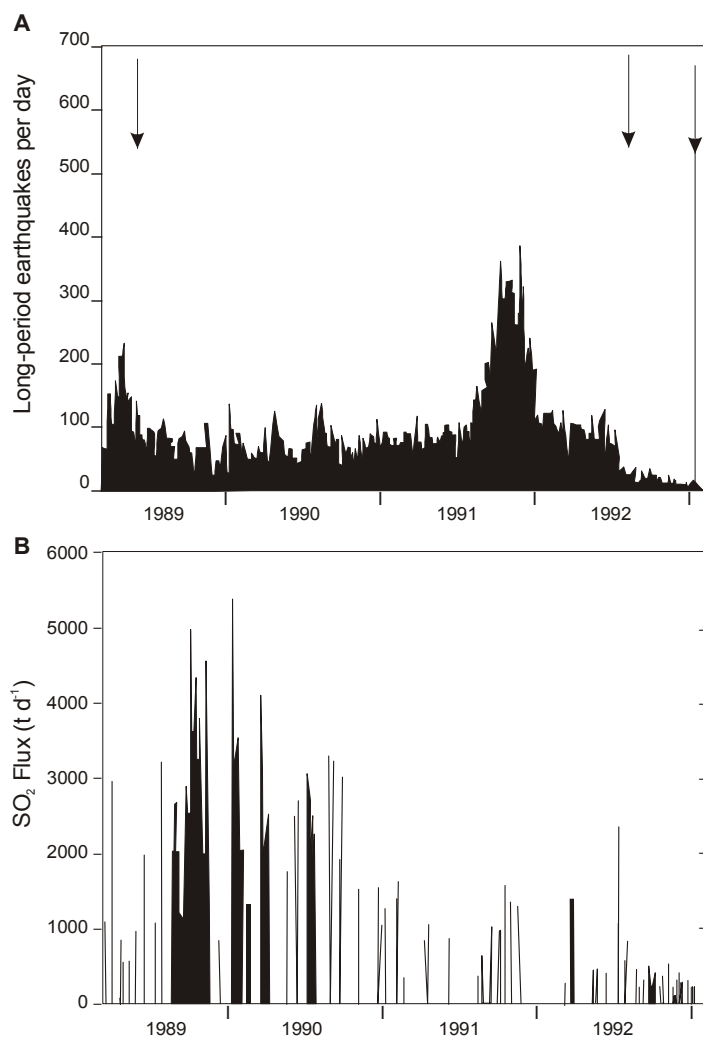


Fig. 17. (a) Plot of SO₂ fluxes from Galeras volcano, Colombia, 1989-1993. Values progressively decline with time. (b) Plot of long-period earthquakes at Galeras during the same time period as in (a) above. The large peak corresponds to rise of magma associated with lava dome emplacement, July-November 1991. Vertical arrows indicate eruptions on 4-9 May 1989, 16 July 1992, and 14 January 1993. From Stix et al. (1993).

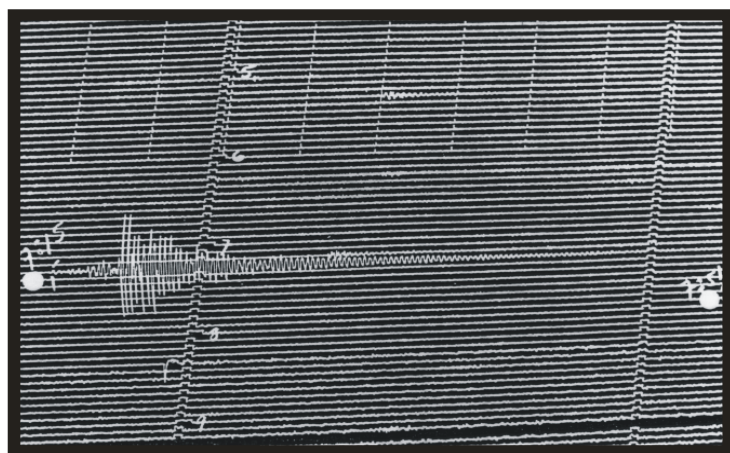


Fig. 18. Monochromatic long-period seismic event recorded by the Crater-2 seismic station at Galeras on 16 July 1992. The duration of the signal is approximately 70 seconds. Note the homogeneous frequency, comparatively small amplitude, and long, slowly decaying coda. These signals have been termed "tornillo" or "screw" events for their resemblance to a threaded screw. Interval between large square-topped ticks is 60 seconds, interval between small ticks is 10 seconds. From Stix et al. (1997).

The 1993 eruptions were remarkable for their clear evidence of pressurization beforehand. Paradoxically, they occurred at a time when parameters such as seismicity, deformation and SO_2 flux were at very low levels. A typical pressurization cycle occurred over a period of days (before the 16 July 1992 eruption), weeks (before the 14 January 1993 eruption), or months (before the 23 March and 7 June 1993 eruptions). A cycle began with the first appearance of monochromatic, low-frequency long-period events, also called “tornillos” or “screws” for their monochromatic frequencies and slowly dissipating character (Fig. 18). SO_2 levels declined during the cycle, while durations of individual tornillos progressively increased, and their dominant frequencies decreased (Fig. 19) (Fischer et al., 1994; Gómez and Torres, 1997; Zapata et al., 1997). These changes are all indicative of gas build up and overpressure beneath the volcano. The cycle was terminated by an explosive vulcanian eruption which released the overpressure by rapid degassing. This degassing could be observed by the high levels of SO_2 immediately after the 23 March eruption (Fig. 19), and by swarms of long-period seismicity which directly followed the eruption (Fischer et al., 1994; Cortés and Raigosa, 1997; Zapata et al., 1997). The high levels of SO_2 and seismicity both dissipated in a matter of hours to days, indicating a return to a comparatively unpressurized state.

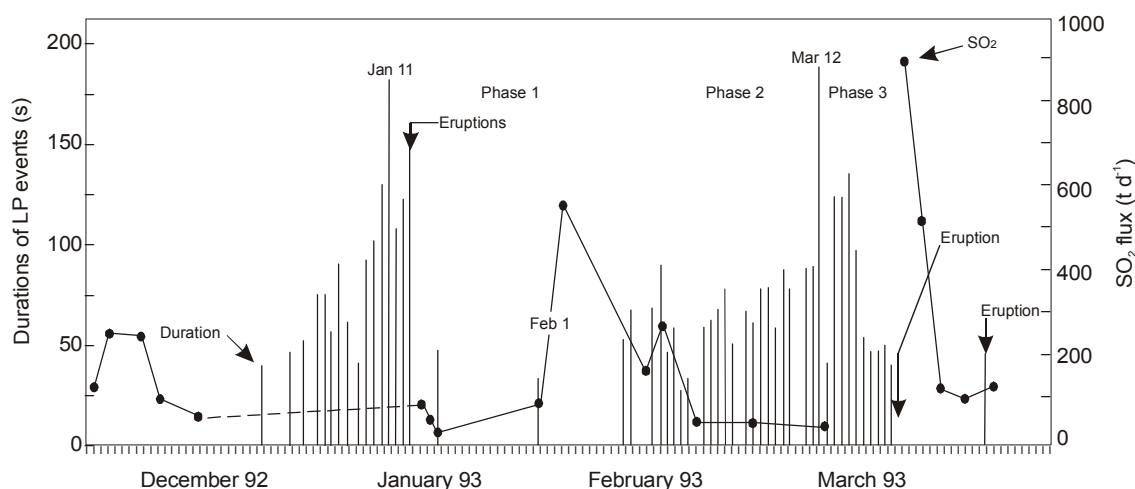


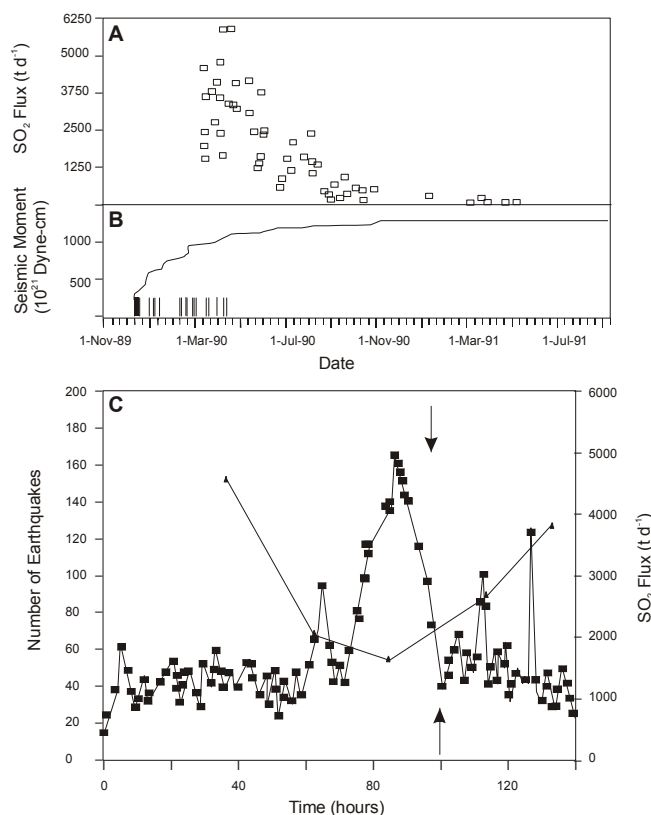
Fig. 19. Plot of SO_2 fluxes (right vertical axis and solid points) and durations of long-period seismic events (left vertical axis and vertical bars) at Galeras, December 1992–April 1993. Eruptions on 14 January, 23 March, and 4 April are indicated. Note low SO_2 fluxes before eruptions and high fluxes afterwards. Durations of long-period events generally increase before the first two eruptions, then disappear afterward. From Fischer et al. (1994).

4.9. Redoubt (Alaska, USA)

Redoubt volcano forms part of the Aleutian volcanic arc. The volcano reactivated in 1989 and was characterized by explosive eruptions in late 1989, followed by dome growth and destruction during the first half of 1990. COSPEC measurements by aircraft were begun in March 1990. Two principal observations were noted. First, an overall decline in SO_2 was observed during 1990–1991 (Fig. 20a), suggesting progressive degassing of a magma body (Casadevall et al., 1994). The SO_2 decrease appears to correlate with a decline in seismicity (Fig. 20b). Second, a decline in SO_2 was noted several days before the 23 March 1990 eruption; SO_2 levels then increased afterward (Fig. 20c). The SO_2 decline corresponds with an increase in

earthquakes, and Casadevall et al. (1994) suggest that the vent was sealed, with a viscous plug forming before the eruption. The two different timescales of SO_2 decline are similar to those observed at Galeras.

Fig. 20. (a) SO_2 fluxes from Redoubt volcano, Alaska, November 1989–July 1991. Note overall decline with time. (b) Cumulative seismic moment at Redoubt during the same time period as in (a) above. (c) SO_2 fluxes (right vertical axis, solid line) and earthquakes (left vertical axis, solid squares and dashed line) at Redoubt, 20–25 March 1990. Vertical arrows indicate eruption on 23 March. From Casadevall et al. (1994).



4.10. Summary comments

It is our firm belief that repeated COSPEC measurements which are closely spaced in time yield valuable information, and we strongly encourage COSPEC researchers to make as many measurements as possible when collecting data. While COSPEC data can be noisy, it is possible to see through the noise by (a) making lots of measurements and (b) using appropriate statistical techniques for filtering purposes (e.g., Connor et al., 1988; Caltabiano et al., 1994).

With sufficiently detailed COSPEC data, it is possible to make correlations with other parameters such as geophysical measurements. Such correlations include:

- seismicity (Mt. Etna (Caltabiano et al., 1994), Arenal (Williams-Jones et al., 2001), Galeras (Fischer et al., 1994; Zapata et al., 1997), Redoubt (Casadevall et al., 1994));
- micro-gravity (Masaya (Rymer et al., 1998; Williams-Jones et al., 2003));
- earth tides (Masaya (Stoiber et al., 1986), Halema'uma'u (Connor et al., 1988), Arenal (Williams-Jones et al., 2001));
- deformation (Mt. St. Helens (Casadevall et al., 1981), Mt. Etna (Bruno et al., 1994));
- lava lake size (Erebus (Kyle et al., 1994)).

Degassing of open magmatic systems, such as Kīlauea, Mt. Etna, and Masaya, appear to be sensitive to variables such as the size of the lava lake, level of magma in the conduit, convection,

and earth tides. While some correlations have been made, more work is needed to better understand these relationships.

There may be a general relationship between low and/or decreasing SO₂ and subsequent explosive eruptions. These trends have been observed at Mt. Etna, Mt. St. Helens, Mt. Pinatubo, Galeras, and Redoubt. The trends appear to be related to pressurization of magmatic-hydrothermal systems which are partially or completely sealed. However, the timescales of sealing and SO₂ decline appear to vary, both for an individual volcano and among different volcanoes, and this aspect is not well understood. Nevertheless, coupled with other information (e.g., seismicity, deformation, micro-gravity), we think that COSPEC measurements can be used to forecast explosive eruptions of this type if (1) a baseline is established beforehand, (2) repeated measurements are made at a sufficiently small time interval, and (3) the COSPEC data are integrated with seismic, tilt, and/or micro-gravity data.

SO₂ and other gases are released both by eruptions and by passive degassing. In some instances, SO₂ is released almost exclusively by explosive emissions, such as in the case of El Chichón in 1982 which released 7 Tg SO₂ (Bluth et al., 1993) and Pinatubo in June 1991 which released 12-20 Tg SO₂ (Bluth et al., 1992; Read et al., 1993; McPeters, 1993). These emissions are, effectively, instantaneous releases of SO₂. In recent years, however, non-eruptive passive degassing from volcanoes also has been recognized as an important mechanism which can release equivalent or greater amounts of gas compared to eruptive emissions. At least two types of passive degassing behavior can be distinguished. (1) Certain volcanoes - e.g., Mt. St. Helens, Galeras, Redoubt, Augustine - show exponential declines of SO₂ over several years (Fig. 21) (Casadevall et al., 1983; 1994; Symonds et al., 1990). Such a trend may indicate the progressive degassing of an isolated body of magma at shallow levels, or a decreased magma supply rate. (2) Other volcanoes, such as Stromboli, Arenal, Masaya, Nevado del Ruiz, and Mt. Etna, maintain high levels of passive degassing over long periods (Fig. 22) (Allard et al., 1994; Williams-Jones et al., 2001; 2003; Stoiber et al., 1986; Williams et al., 1990; Caltabiano et al., 1994). Such large amounts of degassing imply systems which are convective, contain large volumes of unerupted magma, and are open to periodic replenishment of magma. For some of these systems (e.g., Nevado del Ruiz), Williams et al. (1990) demonstrate discrepancies between degassing models, which imply large magma volumes, and deformation models, which suggest small magma volumes. They conclude that these types of magmatic systems are not simple, isolated point-source magma bodies, but rather larger magmatic systems which may have a caldera association.

As a final point, the sources and depths of SO₂ degassing are not fully understood. There is evidence to suggest that SO₂ is released at shallow levels (Gerlach, 1986; Gerlach and Graeber, 1985; Casadevall et al., 1981; Kyle et al., 1994), while other data indicate that SO₂ is derived from magma at deeper levels which is not erupted (Williams et al., 1990; Andres et al., 1991). For example, Nilsson and Peach (1993) have documented low sulphur contents in submarine back arc basin glasses erupted in deep water. Alt et al. (1993) have noted low sulphur concentrations in submarine island arc glasses. Both sets of samples are slightly oxidized and undersaturated with respect to either sulphide or anhydrite. Thus, the low sulphur values may result from deep degassing of volatile-rich magmas.

Another way to reconcile these different viewpoints of shallow vs. deep degassing is by convection which transports deeper, gas-rich magma to shallow levels. At these higher levels, the magma is supersaturated and releases SO₂ and other gases (Kazahaya et al., 1994; Rymer et al., 1998; Williams-Jones et al., 2003).

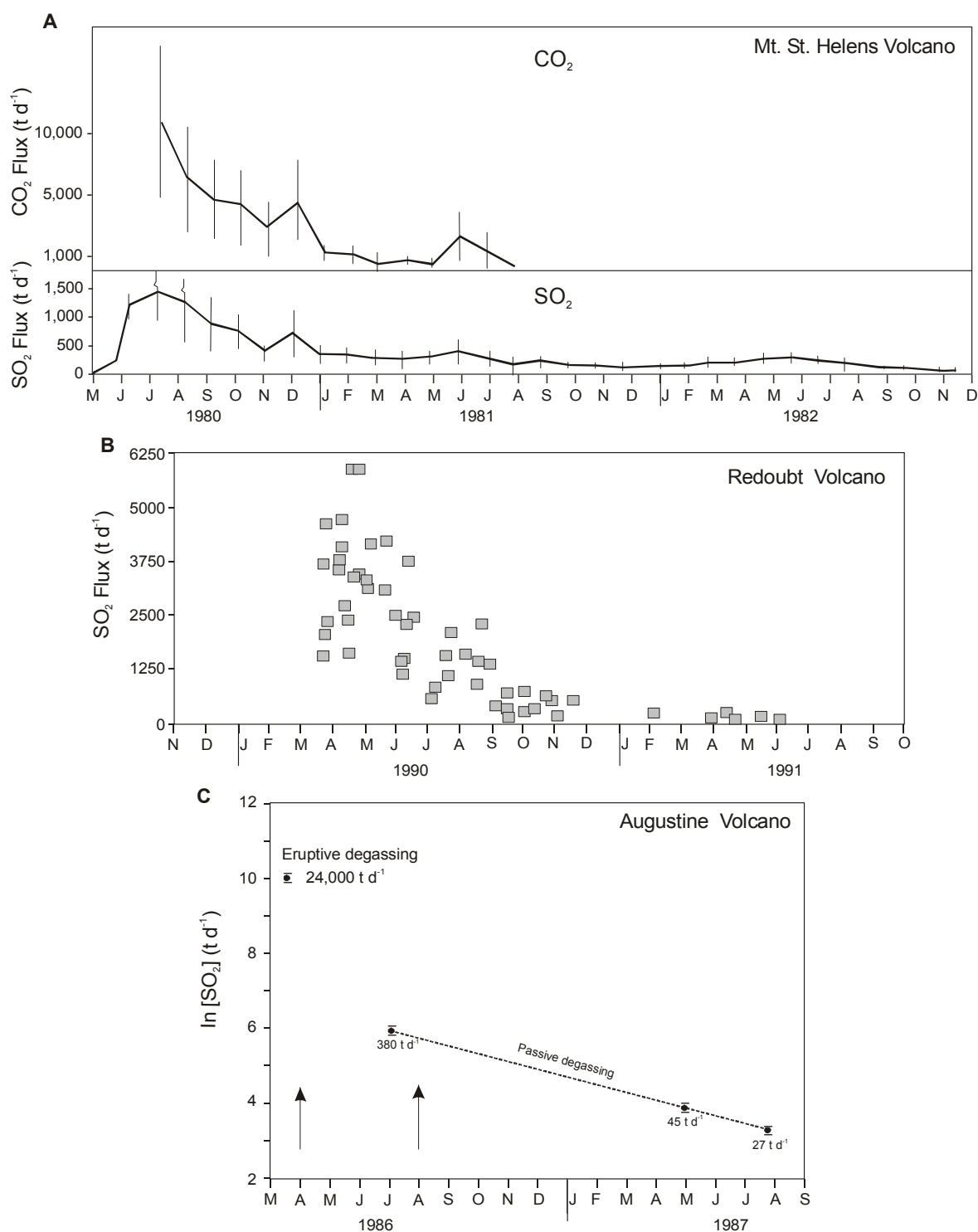


Fig. 21. Three examples of SO₂ fluxes that show progressive declines with time. (a) Mt. St. Helens, May 1980–December 1982. Also shown are CO₂ fluxes. Values in metric tonnes per day. From Casadevall et al. (1983). (b) Redoubt volcano, November 1989–July 1991. From Casadevall et al. (1994). (c) Augustine volcano, Alaska, March 1986–September 1987. Arrows indicate eruptions. From Symonds et al. (1990).

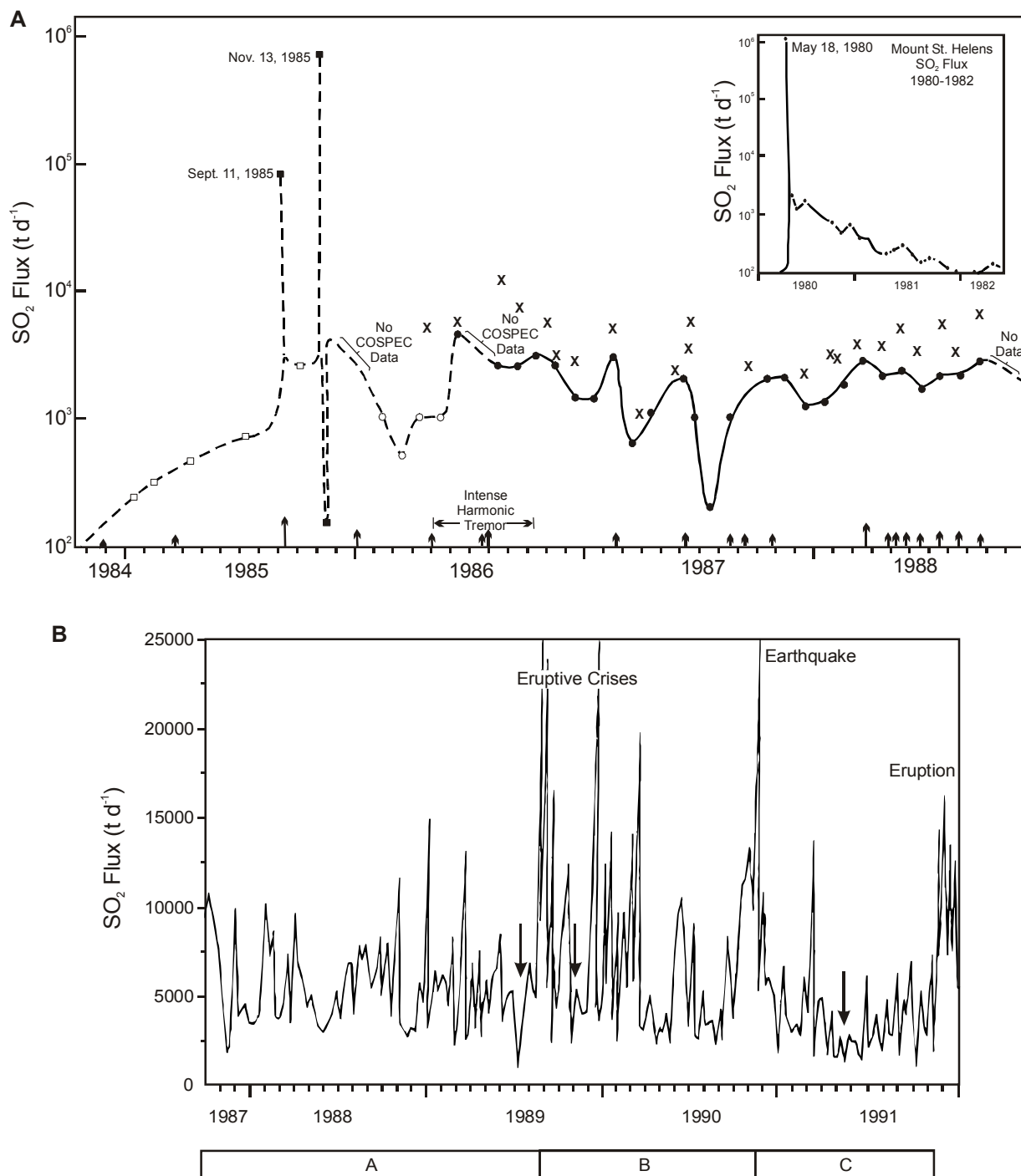


Fig. 22. Two examples of persistently high SO₂ fluxes. (a) Nevado del Ruiz, Colombia, November 1984–November 1988. Sources of data: visual estimates (open squares), TOMS satellite data (solid squares), and COSPEC monthly means (open, solid dots). X's indicate high values recorded each month by COSPEC. Small arrows at bottom of graph indicate notable eruptions or ash emissions. Modified from Williams et al. (1990). (b) Mt. Etna, October 1987–January 1992. Arrows indicate minimum flux values. Horizontal bar at the bottom indicates three different styles of activity: A, quiet summit activity; B, two eruptive periods during September–October 1989 and January–February 1990; C, period prior to the major 1991–1993 southeast flank eruption. From Caltabiano et al. (1994).

5. INTEGRATING COSPEC MEASUREMENTS WITH OTHER GAS DATA

Other measurement techniques and approaches can significantly enhance the value of COSPEC measurements. In this section, we examine four of these approaches, all of which have provided additional information which can be used with COSPEC data: gas infrared remote sensing, gas geochemistry, ash leachate analyses, and melt inclusion petrology.

5.1. *Infrared remote sensing of gases*

Recent advances in infrared technology have led to the development of portable gas correlation radiometers (GASPEC, GASCOFIL) and Fourier transform infrared radiometers (FTIR) which are capable of remotely measuring a variety of gas species. Coupled with the COSPEC, these measurements can provide fluxes and ratios for different gas species. Fluxes are useful for estimating volcanic contributions to the atmosphere for gases such as CO₂ and HCl, which play a role in greenhouse heating and ozone depletion, respectively. Gas ratios can be used in eruption forecasting, since certain gases have different solubilities in magma. For example, HCl is more soluble than SO₂, which in turn is more soluble than CO₂. Thus, fresh gas-rich magma will have high SO₂/HCl and CO₂/SO₂ ratios, whereas progressive degassing over time will lower the gas ratios. While the situation may be more complex for a particular volcano, the basic idea is valid and can provide important information on the state of a magmatic system beneath an active volcano.

Stoiber et al. (1983) have summarized the benefits of remotely measuring gas ratios, in addition to flux measurements:

- the uncertainty of wind speed is eliminated, making the ratio measurements inherently more accurate than flux measurements;
- the pathlength attenuation effects are reduced or eliminated;
- measurements of concentrations (ppm·m) can be made from a stationary point, since information on the wind speed and plume width are not required, and the pathlength is the same for both gas species.

When making the remote measurements, it is important to have an independent verification of gas ratios by direct sampling methods such as fumarole gas geochemistry, Japanese Box alkaline solutions, and/or alkaline filter packs.

Two basic approaches are currently being used to gather simultaneous data from the COSPEC and infrared instruments. The first approach is to calculate gas fluxes with each instrument, then use the two fluxes to calculate a gas ratio. This method has been done by Williams and Dick (1995) using a COSPEC to measure SO₂ and a GASPEC to measure CO₂. This approach is good because the CO₂ flux is measured independently. However, the measurement is inherently difficult, since the sky is used as an infrared source and there is significant CO₂ in the atmosphere.

The second approach uses an artificial or natural infrared source, such as an infrared lamp or a lava dome, to measure the gas between the infrared radiometer and the infrared source. Using this configuration, gas ratios are calculated directly, and fluxes determined indirectly using the COSPEC. This technique was first explored by Notsu et al. (1993) and Mori et al. (1993) who measured the SO₂/HCl ratio by FTIR radiometry at Unzen volcano in March and July 1992, using the hot lava dome as a passive infrared source. They calculated an SO₂/HCl ratio of 0.7-1.9, which agreed reasonably well with direct measurements of gas which gave SO₂/HCl of 1.7 (Hirabayashi et al., 1992). They continued this work at Vulcano in April 1993 using the hot

crater fumaroles as the infrared source (Fig. 23a) (Mori et al., 1995). They calculated SO_2/HCl ratios of 4.9 ± 0.4 , 3.5 ± 0.9 , and 5.8 ± 2.7 for the FA, F47, and lower F21 fumaroles, respectively. These results were 1.5-2.6 times higher than direct fumarole measurements made at about the same time. The high ratios obtained from remote sensing may be caused by preferential dissolution and removal of HCl in the gas, since it is more soluble than SO_2 , or by $\text{H}_2\text{S}-\text{SO}_2$ conversion (Mori et al., 1995).

Francis et al. (1995, 1996a) also measured SO_2/HCl ratios at Vulcano in September 1994, using an FTIR radiometer equipped with an artificial infrared source (Fig. 23b), rather than the natural fumarole source used by Mori et al. (1995). They measured ratios ranging from 0.82 ± 0.17 to 1.37 ± 0.33 (Fig. 24). These values are lower than those found by Mori et al. (1995), although the measurements were made 17 months apart. Using the SO_2/HCl ratios and a COSPEC flux of $19 \text{ t d}^{-1} \text{ SO}_2$, the HCl flux was $14\text{--}23 \text{ t d}^{-1}$. Direct calculations of the flux using the FTIR concentration-pathlength, plume width, and wind speed gave fluxes of $10 \pm 6 \text{ t d}^{-1} \text{ SO}_2$ and $7 \pm 5 \text{ t d}^{-1} \text{ HCl}$ (Francis et al., 1995).

Using an artificial infrared source on Mt. Etna, Francis et al. (1995, 1996a) measured SO_2/HCl ratios from 3.29 ± 0.34 to 4.04 ± 1.62 (Fig. 24). These ratios are higher than those measured by Francis' group on Vulcano (but about the same as the Vulcano ratios of Mori et al. (1995)). Using the ratios and a COSPEC SO_2 flux of $5,500 \text{ t d}^{-1}$ gave an HCl flux of $1,400\text{--}1,700 \text{ t d}^{-1}$ from Mt. Etna (Francis et al., 1995).

Other related work using infrared remote sensing has examined trace gas ratios such as HCl/SiF_4 at Vulcano and Mt. Etna (Francis et al., 1996b), BrO/SO_2 at Soufriere Hills, Montserrat (Bobrowski et al., 2003), COS/CO at Galeras (Stix et al., 1996), and CO/CO_2 and other ratios at Aso volcano, Japan (Mori and Notsu, 1997).

5.2. Gas geochemistry

The analysis of volcanic gas complements and supplements COSPEC measurements in two principal ways. First, the gas analyses allow one to calculate gas ratios which can help unravel the degassing state of a volcano. For example, high S/Cl is indicative of fresh magma, while low S/Cl implies the magma has been degassed. Second, it is possible to make indirect flux estimates of other species such as CO_2 , HCl, and HF by using gas ratios and SO_2 fluxes from COSPEC measurements. For example, given an SO_2 flux of 100 t d^{-1} (50 t d^{-1} equivalent sulphur) and a S/Cl mass ratio of 2, the Cl flux would be 25 t d^{-1} and the HCl flux 25.7 t d^{-1} .

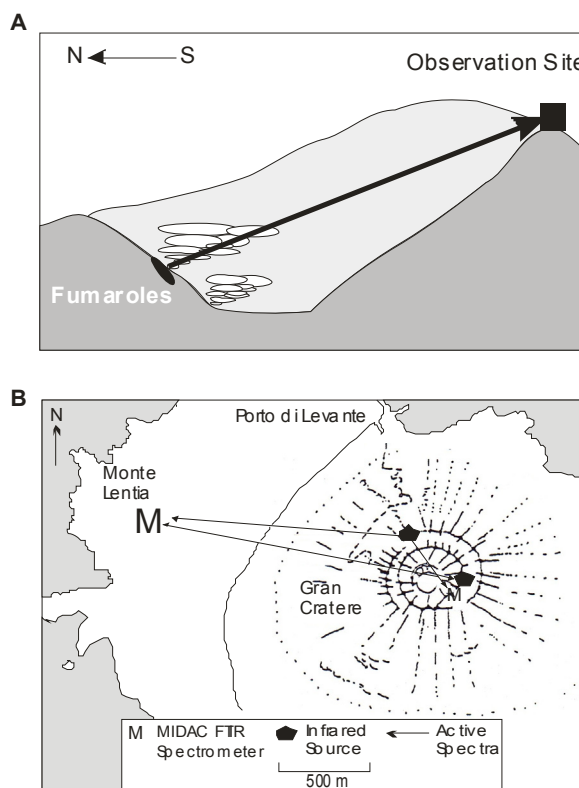


Fig. 23. (a) Sketch of the interior of Vulcano's crater, showing location of fumaroles and FTIR radiometer at rim. From Mori et al. (1995). (b) Sketch map of Vulcano, showing crater, location of infrared source reflectors, and placement of FTIR radiometer in Monte Lentia. From Francis et al. (1995).

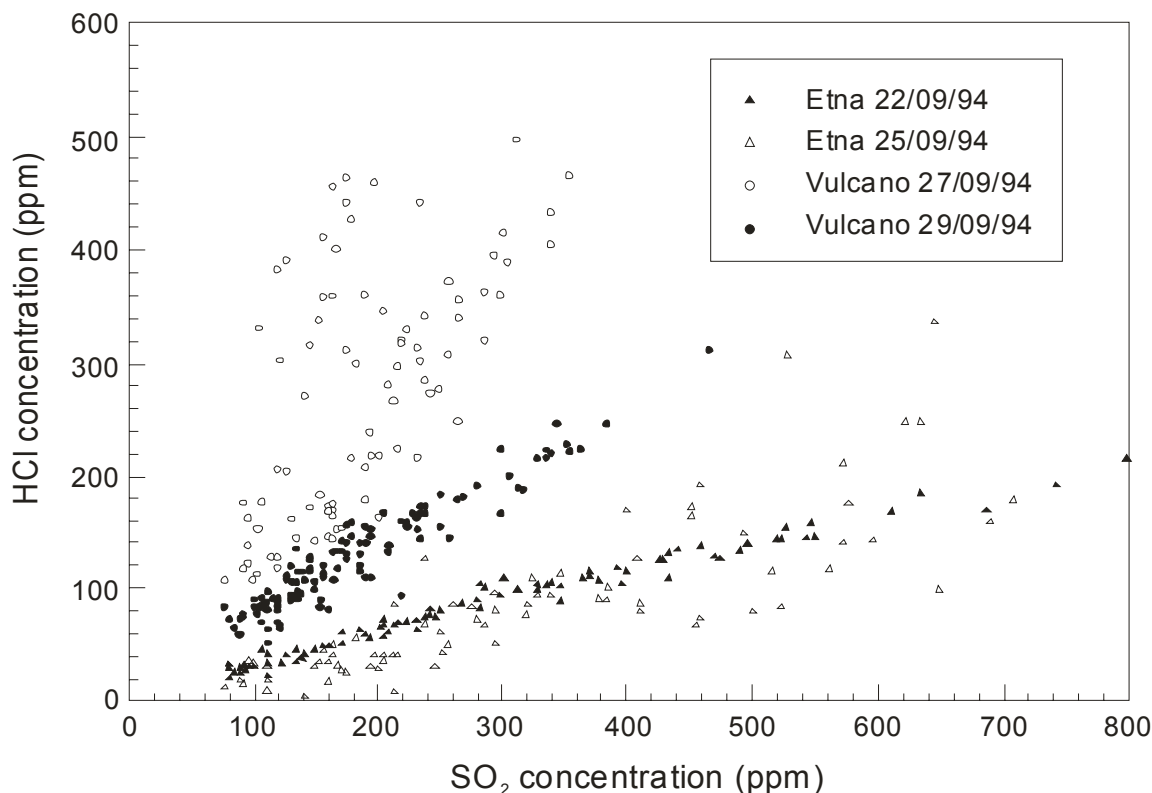


Fig. 24. Plot of SO₂ and HCl concentration-pathlengths (ppm-m) measured by FTIR remote sensing at Mt. Etna (triangles) and Vulcano (circles). Note high SO₂/HCl ratios for Mt. Etna compared to Vulcano. From Francis et al. (1995).

The gas analyses can be obtained several different ways. Crater fumaroles can be sampled directly by collecting gas in evacuated bottles containing alkaline solution (“Giggenbach bottles”) and by condensing the hot gas (Giggenbach, 1975). In general, the hottest, most acid fumaroles are the best for monitoring purposes, since they most closely represent magmatic gas. Also, parameters such as the S/Cl ratio will vary among the different fumaroles. For monitoring purposes, it is important to not average data from different fumaroles, whereas averaging is necessary for flux estimates. In addition to monitoring the S/Cl ratio of fumarolic gas, other useful parameters include the total sulphur, carbon dioxide, and chloride concentrations, the temperature, and the pH. Examples of integrated fumarole-COSPEC work include Augustine volcano, Alaska (Symonds et al., 1990), Stromboli, Italy (Allard et al., 1994), White Island, New Zealand (Rose et al., 1986), and Galeras, Colombia (Goff et al., 1994; Fischer et al., 1997).

If crater fumaroles are not present or are inaccessible, the gas plume can be sampled downwind using Japanese box alkaline traps (Noguchi and Kamiya, 1963), filter packs (Finnegan et al., 1989), Drager/Kitagawa samplers (Allard et al., 1994) and/or Multi-Sensor system (Shinohara, 2005). Using filter pack data collected at Masaya volcano in Nicaragua, Stoiber et al. (1986) made three important observations:

- The S/Cl ratio of gas sampled at the active Santiago crater declined from 1.0 in 1980 to 0.5 in 1982, suggesting progressive degassing of the magma body.
- For a given day, the S/Cl ratio increased from an average of 0.8 at Santiago to an average of 1.6 at Llano Pacaya, which is located 14 km downwind of the crater. This change was probably caused by the greater solubility and/or dry deposition rate of HCl.

- Using average S/Cl ratios from Santiago and the SO₂ fluxes measured by COSPEC, HCl fluxes from Masaya are of the same order of magnitude as the SO₂ flux.

Other studies which have integrated COSPEC and filter pack data include work at Mt. Erebus, Antarctica (Kyle et al., 1990; Zreda-Gostynska et al., 1993), Augustine, Alaska (Rose et al., 1988), and El Chichón, Mexico (Kotra et al., 1983). Lastly, whole-air samples of gas have been taken to study trace gas concentrations from the 18 May 1980 Mt. St. Helens' plume (Inn et al., 1981; Hobbs et al., 1981; Cronn and Nutmagul, 1982; Rasmussen et al., 1982).

5.3. Ash leachates

If volcanic ash from explosive eruptions has not been washed by rain, the ash can be leached to remove soluble elements such as sulphur, chlorine, and fluorine. Analysis of these elements can yield important information which complements COSPEC measurements. The soluble material originates either by solfateric alteration of old rocks in the vent before eruption, or by scavenging of volcanic gas onto the ash surfaces in an eruption column (Taylor and Stoiber, 1973). In the first case, clays, sulphates, and altered rock fragments may be found in the ash. In the second case, the ash frequently will comprise juvenile material, although lithic fragments also can scavenge ash. When the ash is leached before analysis, most elements are removed from the surfaces of the fragments, rather than from within the fragments themselves (Taylor and Stoiber, 1973). Leachates are the best method to detect the presence of fluorine in volcanic gas (Stoiber and Rose, 1973). A brief summary of collection and analysis procedures is given in Table 2.

A compilation of leachate data from different volcanoes is presented in Table 3. For our purposes, the most useful data are the SO₄²⁻, Cl⁻, and F⁻ concentrations and the S/Cl ratio. During the 1963 Irazu eruption in Costa Rica, sulphate and chloride concentrations of leachates were extremely high, and the S/Cl ratio also was elevated (0.65). During the 1974 Fuego eruption, S/Cl values of 3.8 were recorded, also extremely high (Rose, 1977; Stoiber et al., 1978). At Mt. St. Helens in 1980, S/Cl values before the 18 May eruption were low (0.06-0.22), while afterward S/Cl ranged from 0.15 to 1.22, with all but two samples having S/Cl > 0.3 (Stoiber et al., 1980; 1981). During the 19 September 1994 eruption of Rabaul, S/Cl varied from 0.13 to 25; most samples had S/Cl > 1 (Roggensack et al., 1996).

The S/Cl ratio of leachates also can change during the course of an eruption or series of eruptions. During the 18 May 1980 Mt. St. Helens eruption, ash from the directed blast and early fallout had S/Cl > 0.4, while the later fallout near the end of the eruption had S/Cl < 0.4 (Table 3) (Stoiber et al., 1981). During the Rabaul eruption, S/Cl was seen to increase initially, then decrease with time (Fig. 25). At Santiaguito in Guatemala, leachate S/Cl was monitored during 1967-1969, beginning with ash eruptions in May 1967. The leachate S/Cl declined progressively with time (Table 4).

To summarize, leachate data can be used to help deduce the presence of a magmatic gas component during eruptions, in conjunction with other information. In particular, the S/Cl ratio is a valuable indicator, as it is insensitive to dilution effects. It is, however, difficult to establish a threshold between magmatic and non-magmatic S/Cl values, and baseline data is needed for each particular volcano. Nevertheless, explosive eruptions with a magmatic gas component appear to have S/Cl values of 0.1 or higher. Very high S/Cl ratios (> 1) may indicate the presence of mafic magma, with or without magma mixing, and/or a very oxidizing environment (Roggensack et al., 1996).

Table 2. Collection and analysis procedures for ash leachates, modified from Taylor and Stoiber (1973)

1. IN THE FIELD

Collect only fresh ash that has not been rained on.

If ash is falling:

Collect as many samples as time permits, in order to have a temporal record of ashfall. For an individual sample, collect a minimum of 5 g, more for sieving and other purposes. If possible, collect 50-100 g per sample. Collect on a flat inert surface such as a plastic sheet, tarpaulin, space blanket, etc. Transfer ash directly to a clean plastic bag and label bag with sample number, locality, date, and time. Do not handle ash with fingers, as this may result in contamination of C1 and other elements.

If ash has already fallen:

Collect ash from as many localities as possible, to examine spatial variability. For individual localities, identify different tephra layers, then sample each layer. For each sample, collect ash with a plastic spatula or spoon and place ash in a clean plastic bag labeled with sample number, tephra horizon, locality, date, and time. To avoid contamination, do not handle ash with fingers.

2. IN THE LABORATORY

To avoid contamination, never handle ash with hands or fingers; use rubber gloves if necessary. If there is adequate ash, dry sieve using inert mesh (plastic, silk, etc.) to avoid elemental contamination. For simplicity, sieve into 5 fractions: >30 mesh, 30-60, 60-120, 120-230, <230. The 120-230 or 60-120 fractions are normally used for analysis. If only small amounts of ash were collected (e.g., 5-10 g), do not sieve, simply prepare the bulk ash sample for analysis.

For an individual size fraction or ash sample:

Rinse a clean plastic test tube and closure with deionized water and let dry. Weigh the test tube and closure to three decimal places, record weight. Add about 5 g of ash to test tube, then reweigh beaker and record weight. Add about 10 ml of deionized water to beaker, agitate water-ash solution for one hour, then reweigh beaker and record data. Separate solution from ash by decanting solution into a clean test tube; cap test tube to prevent evaporation and set aside. Repeat above steps for test tube with ash, then decant second solution from ash by adding solution to the first solution which has been already separated. Cap test tube to prevent evaporation.

This final solution is the leachate solution to be used for analysis.

3. CALCULATIONS

Example:

SO ₄ ²⁻ concentration in water:	500 ppm
Mass of ash used:	5.136 g
Mass of water used:	20.56 g

$$(500 \text{ ppm} \times 20.56) / 10^6 = 0.01028 \text{ g SO}_4^{2-}$$

$$0.01028 \text{ g SO}_4^{2-} / 5.136 \text{ g ash} = 0.002002 \text{ g SO}_4^{2-}/\text{g ash}$$

$$(0.002002 \text{ g}) \times (10^6) = \mathbf{2,002 \text{ ppm SO}_4^{2-} \text{ absorbed on ash}}$$

4. NOTES

Ash that has been rained on should be avoided, since the rain will have dissolved some or all of the soluble components (e.g., S, Cl) adhering to the ash. For analysis, the same size fraction should be used for all samples if possible, since concentrations of soluble components adhering to the ash will vary as a function of surface area and grain size of the ash. With distance from a volcano, there will be variations caused by various fractionation processes. For example, SO₂ will be oxidized with time to SO₄²⁻. Also, the S/Cl ratio may increase downwind, since Cl is more soluble and thus more easily removed from the gas column compared to S.

Table 3. Average S/Cl ratios for ash leachates from explosive volcanoes

Various Volcanoes, Average S/Cl					
Volcano	Eruption date	S (ppm)	Cl (ppm)	S/Cl	Ref.
Cerro Negro, Nicaragua	1968	67	257	0.26	1
Cerro Negro, Nicaragua	1971	181	777	0.23	1
Pacaya, Guatemala	Oct 1965	868	1240	0.70	1
Pacaya, Guatemala	1968	68	176	0.39	1
Santiaguito, Guatemala	1967-1968	401	977	0.41	1
Fuego, Guatemala	1971	51	189	0.27	1
Fuego, Guatemala	1974	531	140	3.8	1,2
San Miguel, El Salvador	April 1970	1015	7114	0.14	1
Irazu, Costa Rica	March 1963	7249	11160	0.65	1
Nevado del Ruiz, Colombia, Honda	13 Nov 1985	244	1008	0.24	3
Nevado del Ruiz, Colombia, Alto de la Mona	13 Nov 1985	167-267	430	0.39-0.62	3
Mt. St Helens, Washington, USA					
Sample site	Eruption date	S (ppm)	Cl (ppm)	S/Cl	Ref.
ash emission	4 April 1980	37	600	0.062	1
ash emission	12 April 1982	214	980	0.22	1
directed blast, Mossyrock, WA	18 May 1980	1041	1240	0.84	4
directed blast, Randle-Packwood, WA	18 May 1980	935	1620	0.58	4
directed blast, Morton-Randle, WA	18 May 1980	1268	1600	0.79	4
early airfall, Naches, WA	18 May 1980	627	1180	0.53	4
early airfall, Yakima, WA	18 May 1980	347	840	0.41	4
early airfall, Rimrock Lake, WA	18 May 1980	668	880	0.76	4
late airfall, Naches, WA	18 May 1980	147	960	0.15	4
late airfall, Yakima, WA	18 May 1980	67	380	0.18	4
late airfoil, Rimrock Lake, WA	18 May 1980	200	520	0.38	4
airfall, 1300 hrs, Almira, WA	18 May 1980	1322	1040	1.3	4
airfall, 1400 hrs, Almira, WA	18 May 1980	988	1140	0.87	4
airfall, 1500 hrs, Almira, WA	18 May 1980	1041	960	1.1	4
airfall, 1800 hrs, Almira, WA	18 May 1980	1175	960	1.2	4
airfall, 0800 hrs, Almira, WA	19 May 1980	721	1040	0.69	4
airfall, 2200 hrs, Missoula, MT	18 May 1980	931	1200	0.78	4
airfall, 0400 hrs, Missoula, MT	19 May 1980	414	860	0.49	4
airfall, 2320 hrs, Vancouver, WA	12 June 1980	387	820	0.47	4
airfall, 2340 hrs, Vancouver, WA	12 June 1980	387	760	0.51	4
airfall, 0005 hrs, Vancouver, WA	13 June 1980	280	720	0.39	4
ashflow, Spirit Lake, WA	12 June 1980	140	250	0.56	4
airfall, White Pass, WA	22 July 1980	80	150	0.53	4
airfall, White Pass, WA	22 July 1980	57	140	0.41	4
airfall, Toppenish, WA	22 July 1980	80	260	0.31	4

Table 3 continued.

Rabaul, Papua New Guinea					
Sample site	Eruption date	S (ppm)	Cl (ppm)	S/Cl	Ref.
F1, 2 km northwest of Tavurnur crater	19 Sept 1994	397	469	0.85	5
D1, airport terminal	19 Sept 1994	684	5232	0.13	5
D2, airport terminal	19 Sept 1994	494	182	2.7	5
D3, airport terminal	19 Sept 1994	109	93	1.2	5
D4, airport terminal	19 Sept 1994	529	134	3.9	5
D5, airport terminal	19 Sept 1994	519	125	4.2	5
D6, airport terminal	19 Sept 1994	538	109	4.9	5
D7, airport terminal	19 Sept 1994	542	92	5.9	5
D8, airport terminal	19 Sept 1994	604	196	3.1	5
D9, airport terminal	19 Sept 1994	575	205	2.8	5
F7, 2 km northwest of Tavurvur crater	19 Sept 1994	494	20	25	5
D10, airport terminal	19 Sept 1994	602	148	4.1	5
D11, airport terminal	19 Sept 1994	340	182	1.9	5
D12, airport terminal	19 Sept 1994	177	280	0.63	5
D13, airport terminal	19 Sept 1994	239	1242	0.19	5
C9, Matalau	19 Sept 1994	624	360	1.7	5

Notes:

S/Cl ratios are in mass units. Rabaul samples are arranged in stratigraphic order.

References cited: 1: Stoiber et al. (1980); 2: Rose et al. (1982); 3: Williams et al. (1986); 4: Stoiber et al. (1981); 5: Roggensack et al. (1996).

Table 4. Ash leachate analyses from Caliente vent, Santiaguito volcano, Guatemala, May 1967 to April 1969 (modified from Taylor and Stoiber, 1973)

Sample Number	Date	Cl (ppm)	SO ₄ (ppm)	S/Cl
1100	5/10/67	760	1400	0.62
1106	5/14/67	420	1240	0.98
1123	7/21/67	2720	2500	0.31
1500	6/28/68	2800	2800	0.33
1675	1/19/69	880	680	0.26
1951	4/25/69	720	380	0.18
1952	4/26/69	306	184	0.20
1953	4/26/69	280	164	0.20
1954	4/27/69	264	164	0.21

Notes:

Mesh size of ash 115-230. S/Cl expressed as weight ratio.

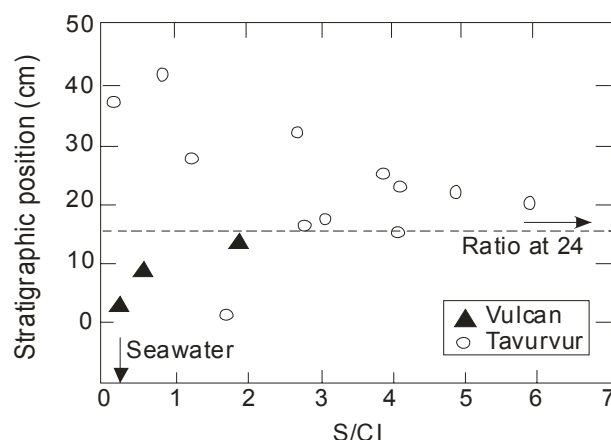


Fig. 25. Plot of ash leachate S/Cl ratios vs. stratigraphic height in tephra erupted from Vulcan and Tavurvur volcanoes, Rabaul caldera, Papua New Guinea, September 1994. Dashed horizontal line indicates depositional break between Vulcan ash below and Tavurvur ash above. From Roggensack et al. (1996).

Increases of S/Cl may occur prior to a major eruption as gas-rich magma begins to ascend and/or lose volatiles. In this case, contemporary COSPEC measurements may show increased SO_2 fluxes. Increases in S/Cl during an eruption (e.g., Rabaul 1994) may indicate the involvement of more mafic magma and/or magma mixing. Decreases of S/Cl over the course of an eruption (e.g., Mt. St. Helens 18 May 1980) or a series of eruptions (e.g., Santiaguito 1967-1969) may track magma degassing from initially sulphur-rich to sulphur-poor. Simultaneous COSPEC measurements may show declining SO_2 fluxes.

In addition to the S/Cl ratio, the absolute concentrations of SO_4^{2-} , Cl^- , and F^- may provide useful information. Elevated concentrations may indicate high gas pressures, mafic magma, and/or a long residence time in the crater (Taylor and Stoiber, 1973).

Finally, knowing the sulphate concentrations of ash leachates and the volume of ash erupted allows one to calculate the amount of sulphur which has been scavenged from the eruption column (Taylor and Stoiber, 1973). For example, Stoiber et al. (1981) measured an average of 500 ppm sulphur in ash leachates from the 18 May 1980 eruption of Mt. St. Helens. Using an independent estimate of the mass of ash erupted (488 Tg), they calculated that at least 0.24 Tg sulphur was scavenged during the eruption. This is a minimum estimate of the sulphur released by an eruption, since much if not most gas remains as a free gas phase. The leachate estimate can, however, be compared to other estimates from COSPEC, TOMS, and melt inclusion measurements.

5.4. Petrology and geochemistry of melt inclusions

Petrologic methods can be used to independently estimate the amount of sulphur released by an eruption. During magma crystallization, small blebs of melt are trapped within growing crystals. These blebs form melt inclusions which can provide information on the sulphur content (and other elements) of a magma prior to an eruption. During the eruption, the magma releases SO_2 and other gases. The matrix glass in a pumice or scoria fragment contains the sulphur content of the degassed magma. The sulphur concentrations in melt inclusions and matrix glasses are measured by electron microprobe analysis. The difference in sulphur concentrations between melt inclusions and matrix glasses is, theoretically, the amount of sulphur lost during the eruption. The equation is as follows:

$$(13) \quad \text{SO}_2 = (\Delta S M g 2)/10^6$$

where SO_2 is the amount of SO_2 released by the eruption in tonnes, ΔS the difference in sulphur concentrations (ppm) between melt inclusions and matrix glasses, M the dense rock equivalent (DRE) mass of magma ejected by the eruption in tonnes, and g the weight fraction glass in the rock. The factor 2 converts sulphur to equivalent SO_2 . To use the petrologic approach requires careful study of the different melt inclusion populations.

It is generally acknowledged that petrologic calculations are minimum estimates and should be recognized as such. Therefore, they must be used with care and concurrently with other methods, discussed above. There are five basic problems with the petrologic approach:

1. The technique considers only degassing of magma which has been erupted, not unerupted magma which also may degas.
2. Along related lines, passive degassing of magma is not considered.
3. Sulphur contents of melt inclusions are frequently significantly lower than the solubility limit, implying that the magma had been partially degassed prior to entrapment of the melt inclusions.
4. Sulphur concentrations in melt inclusions also can be variable, raising the question of which melt inclusions are representative of the pre-eruptive magma. Sources of this variability include sequential crystallization, volatile stratification within a magma body, mixing of magma by convection, and mixing of two different magmas. For example, melt inclusions from the upper part of a magma body may be sulphur-poor, while deeper levels may be sulphur-rich. The different levels may mix, or the lower levels may never get erupted.
5. The sulphur is assumed to be entirely dissolved in the magma before eruption. In certain cases, however, part of the sulphur may accumulate in a separate aqueous fluid phase, which cannot be estimated by the petrologic method. The presence of a fluid phase can explain both the low and variable sulphur contents of melt inclusions and the large sulphur output from many explosive eruptions.

The petrologic method appears to work best for open systems, i.e., those that are frequently replenished by fresh magma. For example, Arenal volcano in Costa Rica has been continuously degassing since it re-activated in 1968. According to COSPEC measurements, the volcano has released about 1.3 Tg SO_2 between 1968-1996. By comparison, petrologic calculations indicate that 0.4-0.8 Tg SO_2 was released during this time (Williams-Jones et al., 2001). This estimate is about 2-3 times less than the COSPEC estimate. By contrast, closed systems may have more isolated magma bodies which are infrequently replenished. In such cases, the difference between the petrologic approach and other methods may be extremely large. For example, the 15 June 1991 eruption of Mt. Pinatubo released 12-20 Tg SO_2 according to remote sensing measurements (Bluth et al., 1992; Read et al., 1993; McPeters, 1993). Since melt inclusions had lower sulphur contents than matrix glasses, petrologic calculations indicate that no SO_2 was released (Westrich and Gerlach, 1992; Gerlach et al., 1996), which is clearly wrong. Similarly, COSPEC, TOMS, and ash leachate data suggest that 0.5-2.2 Tg SO_2 were released by the 18 May 1980 Mt. St. Helens eruption (Millán et al., 1985; Bluth et al., 1993; Stoiber et al., 1981), while petrologic calculations indicate a release of only 0.08 Tg SO_2 (Gerlach and McGee, 1994). Other examples include Lascar and Lonquimay in Chile (Andres et al., 1991) and Redoubt (Gerlach et al., 1994).

We therefore urge extreme caution when calculating SO_2 releases using petrologic methods. Prior to eruption, the sulphur is not simply dissolved in magma. It may be contained in a fluid phase or anhydrite (e.g., Gerlach et al., 1996; Fournelle, 1990), and it may be released by

intrusive magma (Williams et al., 1990), by more mafic magma at deeper levels (Andres et al., 1991), and/or by convective degassing (Kazahaya et al., 1994).

Perhaps a more fruitful way to use the petrologic equation is to take an inverse approach (Williams et al., 1990). For example, by knowing (1) the amount of SO₂ released using COSPEC or other methods and (2) the original sulphur concentration in the magma from melt inclusion and/or sulphur solubility data, one can calculate the total amount of magma required to degas the volcano. The approach assumes that all the sulphur originated from the magma. This information can be valuable in estimating the size of the magmatic system associated with an active volcano.

6. CONCLUDING REMARKS

This chapter has provided a summary of COSPEC and related studies on active volcanoes, as well as some information bearing upon the behavior of sulphur in volcanic environments. As such, it is intended to be a reference source for COSPEC research. The value of COSPEC measurements is significantly enhanced if other datasets and information are incorporated into an interpretation of how a volcano accumulates and loses gas. Ultimately, the combined data help develop an overall model of how the volcano works.

We hope that the reader will be able to use the information contained herein in a practical manner. Many new applications and approaches using the COSPEC are being tried, and we encourage the reader to explore new possibilities that we have not discussed.

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