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Monitoring gases from andesite volcanoes

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Monitoring gases from andesite volcanoes for hazard mitigation or scientific enquiry is complicated by the wide range of eruption styles. Monitoring is aimed at both measuring the rates of gas emission, and changes in their compositions. Direct sampling techniques are restricted to accessible vents, and are unsuitable for syn-eruption monitoring. Correlation spectroscopy is a simple and robust method for measuring emission rates of sulphur dioxide, but is subject to large errors. Open-path Fourier transform spectroscopy provides a remote method for determining plume gas compositions, but requires careful atmospheric radiative transfer modelling. Few andesite volcanoes have been consistently monitored. Published data show that there is no simple general model for volcano degassing: each volcano, and each eruption, presents separate problems, many of them arising from the evolving interaction between magmatic and hydrothermal systems during an episode of activity. Because of its lower solubility in magmas and conservative behaviour in hydrothermal systems, remote measurements of carbon dioxide proportions and emission rates would be extremely valuable for monitoring, but they remain difficult because of its high atmospheric concentration.

Keywords: volcano degassing; gas monitoring techniques; dome-building eruptions

1. Introduction

Silicic magmas erupt in a wide range of styles, ranging from passive extrusion of lavas through peléan dome growth to Plinian explosive eruptions. As the current eruption of the Soufrière Hills volcano demonstrates, the interplay between crystallization, viscosity, gas content and pressure dictates that a magma body may be extremely sensitive to small changes in conditions, leading to widely different eruption outcomes, and thus to the hazards presented. It is the variability in mechanisms and timing of gas release that makes andesitic eruptions so diverse, and thus interesting to volcanologists. In this paper, we interpret terms such as 'andesitic eruption' and 'andesite volcano' loosely, to include all silicic dome-building eruptions at convergent plate settings.

Gas monitoring at andesite volcanoes has two related motives: first, to contribute to risk mitigation by identifying potentially hazardous developments in quiescent or active volcanoes, and, second, to obtain a more complete understanding of the role of gases in volcanic systems. Progress towards the first, pragmatic, goal also requires progress towards the second, more abstract, goal. In addition, two related

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† Deceased.

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methodologies are involved: to quantify the rates and amounts of gases erupted, and to characterize their compositions. The former can present more serious practical difficulties than the latter. Excellent progress has been made in recent years in developing models for crystallization and degassing of magmas. Such models need to be tested against field data that can only be obtained by volcano monitoring.

Because eruptions of silicic magmas present greater hazards than those of basaltic magmas, the opportunities for sampling gases safely are far more limited. Necessarily, most detailed studies have been carried out on quiescent fumaroles before or after major eruptions, raising questions about how to distinguish the magmatic gas signature from that of a related hydrothermal system. In fact, many studies of gases from andesite volcanoes have been concerned precisely with understanding the interactions between magmatic and hydrothermal systems over sustained periods (Fischer *et al*. 1996). Direct observations of active eruption plume gases are rare, but modern remote sensing techniques offer hopes of obtaining better data. In this paper, we assess the existing techniques for monitoring gases; summarize observations and interpretations made at some key volcanoes (focusing on dome-building eruptions); and comment on the future potential of volcanic gas monitoring.

2. Techniques for monitoring gases from andesite volcanoes

(*a*) *Direct sampling techniques*

These have been employed since Davy first collected gases in wine bottles on Graham Island in 1831. Modern sampling methods include use of filter packs, Giggenbach bottles and condensing systems. Collected material is subsequently analysed using a wide range of standard gravimetric, chromatographic, spectroscopic and isotopic techniques. These approaches have been usefully reviewed by Le Guern (1983) and Symonds *et al*. (1994).

While these techniques are capable of delivering precise data and provide the foundation for all volcanic gas studies, they are subject to a number of limitations.

(a) Only vents that can be approached safely can be sampled, usually restricting gas sources to subordinate, relatively low temperature vents.

(b) On sampling, the identity of original gas species and their oxidation states may be obscured due to reactions with reagents, and with the material of the containers. Thus, H_2S, S and SO_2 may all be reported as SO_2 or sulphate. However, thermochemical restorations may be performed to infer original gas compositions, redox conditions and temperatures, in order to provide more comparable data from one volcano to the next (Symonds *et al*. 1992; Gerlach 1993).

(c) Sampling problems dictate that routine monitoring of eruptions is impractical. Most published data are based on either a single sampling campaign, or on samples widely spaced in time.

Aircraft have also been used to sample plumes directly, using on-board filter packs and optical spectrometric techniques such as the MIRAN and LI-COR analysers for CO_2 (Gerlach *et al*. 1997), and closed-path FTIR spectrometers for SO_2 and other gases (Gerlach *et al*. 1998). Aircraft are notoriously expensive to operate, however, limiting the frequency of operations. They are also impractical for sampling major, ash-laden eruption plumes.

An alternative solution to conventional direct sampling, which has not yet become widespread, is the use of automated continuous recording electrochemical sensors. McGee & Sutton (1994) reported use of this technique at Mt St Helens, where they used a sensor that detected undifferentiated reducing gases. Modern solid state sensors have been also been used successfully at Vulcano, Italy, for sustained monitoring of CO_2, SO_2 and H_2S at the ppb level, with telemetry of data to an observatory (M. Valenza, personal communication). Although susceptible to destruction during the course of a major eruption, such sensors are currently the only means of collecting continuous gas data.

(*b*) *Ground-based remote sensing techniques*

Much remains to be done to explore the full potential of the range of modern remote sensing techniques. Their major advantage over conventional techniques is the fundamental issue of safety. They have many other advantages, however. First, they are non-intrusive, eliminating the possibility of secondary reactions, contamination or condensation of volatile fractions during sampling. Second, since data are transferred directly from sensor to a computer, plume gas concentrations may be available in near-real time. This is an important issue for monitoring, given that conventional sampling techniques involving ‘wet chemistry’ may take days or weeks to complete. Finally, remote sensing permits observations of even the most intense phases of activity, not accessible to other means.

Here we review the two main ground-based remote sensing techniques that have been used to monitor volcanoes: we omit several other techniques which have been used on an experimental basis.

(i) *COSPEC (correlation spectroscopy)*

The COSPEC, initially designed for monitoring environmental SO_2, has been a standard tool for volcano monitoring since it was first used in 1971 at Mt Mihara, Japan (Stoiber *et al*. 1983). It contributed significantly, for example, to the successful forecasting of the massive June 1991 eruption of Mt Pinatubo: with the onset of seismic unrest, SO_2 emissions which increased by tenfold over two weeks identified that magma was involved, and rising, and that eruption could be imminent (Daag *et al*. 1996; Punongbayan *et al*. 1996). Additionally, COSPEC-derived SO_2 emission rates have provided the reference against which global volcanic contributions of CO_2, and other gases, to the atmosphere have been estimated (Williams *et al*. 1992). Essentially, the instrument measures the absorption by SO_2 molecules of scattered solar UV radiation passing through the plume, converting this to concentration information by calibration against standard SO_2 reference cells. Volcanic SO_2 flux estimates are made by coupling this information with wind speed measurements. Symonds *et al*. (1994) provide a useful summary of the technique.

COSPEC has several advantages for routine volcano monitoring: it is portable; uses the Sun as a natural source of UV radiation; does not require precise pointing; can operate even through overcast skies; has modest power requirements and does not require specialist technicians for operation. As a robust and practical method to make quantitative estimates of the SO_2 emissions, it can provide a useful measure of

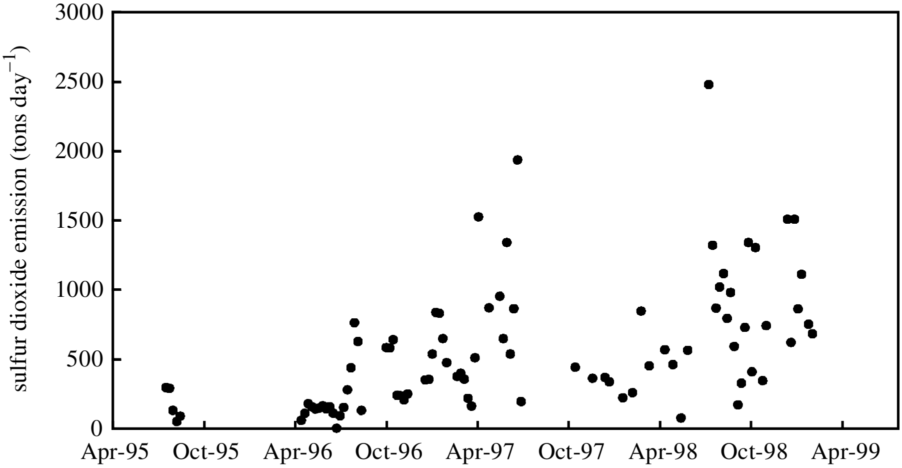

Figure 1. Weekly averages of SO_2 emission rates, Soufrière Hills volcano, Montserrat, obtained by road, boat and aircraft traverses. The number of traverses averaged varies widely, with no data on some days. As is typical of COSPEC data, there are wide variations between data points, but an overall increase through time is evident, as is the fact that emissions remained high after the cessation of dome extrusion in March 1998. Highest values often followed major dome collapse events.

the overall level of activity of a volcano. In conditions such as those at Montserrat, where the volcano is often shrouded by cloud for weeks at a time, routine COSPEC measurements may provide a proxy for the rate of magma extrusion (Young *et al.* 1998).

The chief disadvantage of the COSPEC is that it is a rather blunt tool: cumulative errors range between 15 and 40% (Stoiber *et al.* 1983). COSPEC datasets are thus typically noisy, and large amounts of data are required to identify significant trends (figure 1). The largest source of error lies in obtaining good wind data. Aircraft traverses provide the best results, since the aircraft navigational equipment can be used to derive wind speeds directly.

Furthermore, in some situations, such as the 1992 Mt Spurr eruption, the emission rate of SO_2 may not be a reliable indicator of the level of volcanic activity, as SO_2 can be scrubbed by hydrothermal systems through which gases are released (Doukas & Gerlach 1995). Alternatively, where gas is released into humid atmospheres, rapid conversion of plume SO_2 to sulphate aerosol may decrease the SO_2 burden measured by COSPEC.

COSPEC faces a more fundamental limitation, however, which is that new instruments are no longer manufactured, and spare parts are rarely available.

(ii) *OP-FTIR (open-path Fourier transform infrared spectroscopy)*

Initially developed for laboratory and industrial applications (Brown *et al.* 1992), OP-FTIR spectrometers are now available as small, field portable instruments suitable for a wide range of applications, e.g. detecting battlefield chemical weapons. Owing to the broad spectral range (4200–400 cm^{-1}; 2.4–25 μm) used in OP-FTIR spectroscopy, a diverse variety of gas species can be analysed simultaneously. Mori *et al.* (1993, 1995) first applied the technique to volcanology at Mt Unzen, Japan, during

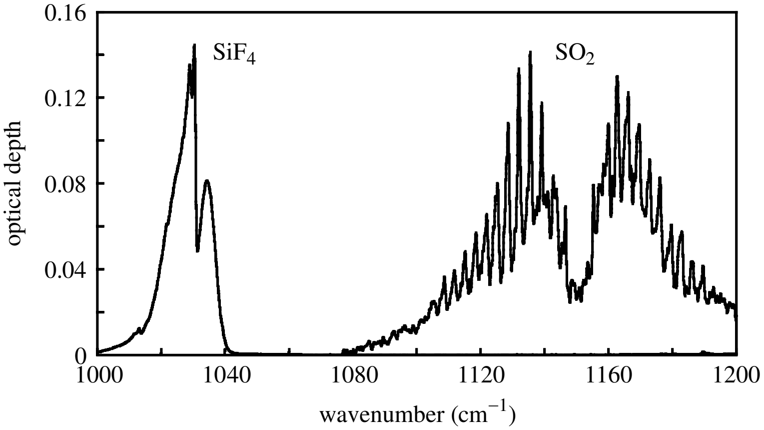

Figure 2. Reference absorbance spectra of SiF_4 (16 ppm m) and SO_2 (125 ppm m), showing the strong and distinctive absorption feature of SiF_4.

its recent eruption, and later to Vulcano. In studies on Mt Etna and Vulcano since 1994, Francis *et al*. (1995, 1998) demonstrated that long-path FTIR spectroscopy could be conveniently used to obtain consistent SO_2:HCl plume ratios at distances of up to 12 km.

The technical aspects of FTIR spectroscopy applied to volcanology are discussed by Oppenheimer *et al*. (1998). Its chief merit is its flexibility. Several sources of infrared radiation can be employed: artificial lamps, hot rocks on the volcano itself, the Sun, and exceptionally the Moon (Burton *et al*. 2000*a*). Near-real time analyses with high temporal resolution are also possible. Most of the volcanically important gases have been detected: H_2O, SO_2, CO_2, CO, COS, HCl, HF (Burton *et al*. 2000*b*; Mori & Notsu 1997). H_2S has not been detected to date because detection limits are rather high for this gas: it follows that H_2S:SO_2 ratios and redox conditions have not been measured.

In a field experiment, Francis *et al*. (1996) discovered unexpectedly that the trace gas SiF_4 could be detected easily thanks to its strong absorption band at 1032 cm^{-1} (figure 2). This gas had not hitherto been reported in volcanic gases because it cannot be distinguished from HF in conventional analyses, although under homogeneous equilibrium conditions SiF_4 should follow CO in order of abundance (Symonds *et al*. 1992). Thermodynamic considerations show that the HF:SiF_4 ratio increases sharply with increasing temperature. Thus, remote measurements of SiF_4 offer a way of constraining fumarole temperatures.

While most FTIR studies have measured absorption by gases of infrared radiation from warm sources, Love *et al*. (1998) showed that it is also possible to measure gas infrared emission spectra, using a cold sky background. They measured SO_2:SiF_4 ratios in the plume from Popocatapetl volcano, Mexico. Over three days before ash eruptions on 25 and 26 February 1997, SO_2:SiF_4 gradually increased, rising steeply immediately after the explosion (figure 3). Counter-intuitively, this observation suggests *cooling* of gas before the explosion. Love *et al*. speculated that this might be due to rapid adiabatic expansion of gas in response to a sudden reduction in pressure as a plug in the conduit gave way.

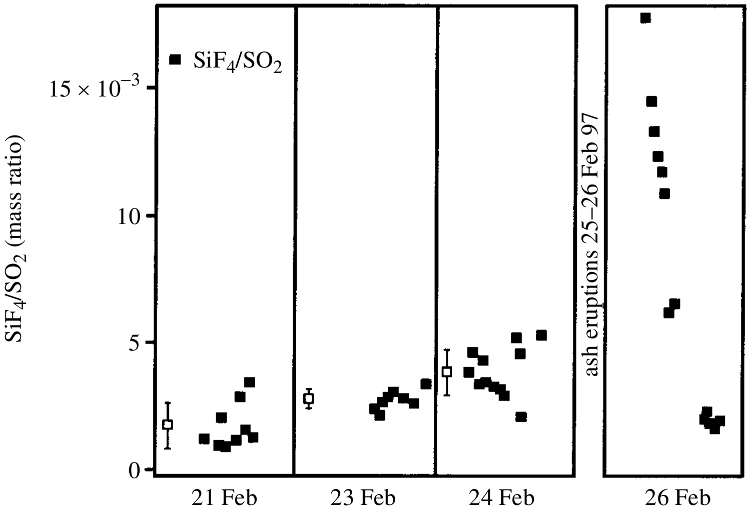

Figure 3. SiF_4:SO_2 ratios measured by OP-FTIR in plume at Popocatepetl in 1997. The SiF_4:SO_2 ratio increased gradually before ash eruptions, indicating reducing gas temperatures, interpreted to be caused by adiabatic gas expansion. Adapted from Love *et al*. (1998).

Although FTIR spectrometry clearly provides a powerful new tool, it is not a panacea for several reasons:

(a) The equipment is less easily portable than the COSPEC. While the Sun provides an intense source of infrared radiation, it can be difficult to contrive a suitable arrangement such that one views the Sun through the plume.

(b) Data retrieval can be complex. Working over short path lengths (100–200 m) using artificial lamp sources provides the simplest data to analyse, but is often not practical. Since viewing the Sun involves an optical path through the whole thickness of the atmosphere, careful radiative transfer modelling is required.

(c) Given their high ambient concentrations, CO_2 and H_2O present particularly difficult measurement challenges. Absorption by CO_2 and H_2O across a number of spectral regions may also prevent analysis of other gas species within these regions.

(d) Comparisons with conventional analytical techniques may be difficult because FTIR reports column amounts of individual gas phase molecular species. For example, column amounts of SO_2 but not sulphur may be retrieved by FTIR, whereas conventional analyses variously report some or all of SO_2, H_2S, sulphate, and sulphur.

(e) Perhaps most importantly, while OP-FTIR techniques provide access to major eruption plumes which are inaccessible to conventional sampling, soluble gases such as HCl and SO_2 may be scavenged from the plume into condensing water vapour at widely different rates. This is an area of research which is newly opening up. OP-FTIR studies promise to contribute not only to understanding of volcanic systems, but also to broader questions of tropospheric chemistry.

(c) Satellite remote sensing of volcanic gases

Although designed for an entirely different purpose, considerable success has been achieved in using the total ozone mapping spectrometer (TOMS) on the Nimbus-7 and Meteor-3 satellites to map the atmospheric distribution of volcanic SO_2. Primarily designed to determine ozone concentrations by measuring back-scattered solar ultraviolet irradiance in six narrow wavelength bands, TOMS is able to take advantage of strong absorptions by SO_2 in the same part of the spectrum to measure SO_2 concentrations. TOMS provides a best pizel resolution of 47 km at nadir, but averages 62 km. Thus, while it is well-adapted to obtaining estimates of bulk SO_2 from large dispersed plumes, its footprint is too large to permit observations of volcanoes such as Soufrière Hills, Montserrat, whose SO_2 emission rate is typically less than 1000 t d^{-1}. Bluth *et al.* (1993) estimated that TOMS successfully detected SO_2 from 55 out of 350 known eruptions between 1979 and 1992, and also identified several eruptions not known from ground studies.

Limb-sounding instruments (which look obliquely through the atmosphere, rather than straight down at the ground) are capable of detecting trace gases at much lower concentrations than the nadir-pointing TOMS, but the footprints of these sensors are inevitably even larger. The microwave limb sounder (MLS) aboard the Upper Atmosphere Research Satellite (UARS) began operating 100 days after the June 1991 eruption of Mt Pinatubo, and immediately detected SO_2, with peak mixing ratios of 15 ppbv (parts per billion by volume) near 26 km altitude. An initial input of 17×10^6 t was estimated compared with the 20×10^6 t estimated from TOMS (Read *et al*. 1993). Although superior to TOMS in resolution, detecting SO_2 down to mixing ratios of 1–5 ppbv, the MLS is also sensitive only to gas at altitudes greater than 15 km, so tropospheric gas is inaccessible.

It is hoped that developments in satellite-based technologies will soon provide widespread capability for remote sensing of even small volcanic SO_2 plumes. Airborne infrared (TIMS) measurements of SO_2 (Realmuto *et al*. 1997) are convincing steps in this direction, towards the long-term goal of replacing routine COSPEC monitoring with SO_2 measurement from space.

3. Gas data from some selected andesite volcanoes

Published investigations of gases from silicic volcanoes are diverse in quality, methodology and purpose. Table 1 summarizes some of the most representative analyses. Given the wide range of sampling and analytical techniques, it can be difficult to make comparisons between different datasets. We present here the salient points arising from some recent studies, and comment on their implications.

(a) Mt St Helens, USA: post-eruptive degassing, magma ascent and crystallization

Following the 18 May 1980 dacite eruption of Mt St Helens, COSPEC measurements, aircraft plume sampling, and direct sampling of high-temperature lava dome fumaroles were used to study gas chemistry and emission rates over the following seven years.

A total of 2 Mt of sulphur dioxide was erupted over the period 1980–88, including the climactic 18 May eruption. Of this, only 0.08 Mt could be accounted for from melt inclusion data, indicating the presence of a saturated vapour phase at depth (Gerlach & McGee 1994). During the first year after the 18 May eruption, the proportion of H_2O in the fumarole gases increased linearly, while fumarole temperatures and both CO_2 and SO_2 emissions decreased. The peak SO_2 emission rate, however, was actually in July 1980, two months after the major eruption (Casadevall *et al*. 1981, 1983). Reduced gas and sulphur dioxide emissions showed significant increases before each of four dome-building episodes since mid-1984. According to McGee & Sutton (1994), increased degassing became detectable when fresh upward moving magma reached levels between 2 km and a few hundred metres beneath the dome, between 60 and 12 h before surface extrusion of lava.

Although SO_2 was dominant in plume gases, redox calculations show that H_2S was the dominant magmatic sulphur species below depths of about 200 m, with oxygen fugacity near the nickel–nickel oxide buffer (NNO). Decreasing proportions of CO_2 and S, and increasing H_2O during 1980–81 indicated volatile depletion of a single magma batch (Gerlach & Casadevall 1986). Concurrent studies of CO_2 (MIRAN) and SO_2 (COSPEC) emissions allowed Harris & Rose (1996) to identify two gas components during open-vent conditions in the five months following the climactic eruption. The first, characterized by a low CO_2:SO_2 mass ratio of 1.7, had a flux which decayed proportionally to the inverse square root of time and was related to crystallization of a large stationary magma body at depth. The second, characterized by a high CO_2:SO_2 mass ratio of 15, caused short-lived peaks of high CO_2 flux, due to episodic release of gas from parcels of magma ascending to replenish the static magma body.

(*b*) *Mount St Augustine Volcano, Alaska:* Cl-*rich gases*

Kodosky *et al*. (1991) studied Augustine fumarole gas compositions between 1979 and 1984 and noted a marked increase in H_2O and a decrease of both CO_2 and HCl over this period; trends similar to those observed at Mt St Helens after the May 1980 eruption. They attributed these changes to a decline in the magmatic volatile fraction, coupled with an increasing proportion of seawater in the emissions. They used mass balance calculations to infer that degassing of eruptive products and near-surface magma could account for all of the HCl and SO_2 degassed from Augustine, and concluded that any Cl and S derived from near-surface sources must have entered the system before extensive magmatic crystallization.

During the short-lived 1986 andesitic dome-building eruption, airborne COSPEC observations and filter pack sampling on 3 April revealed sulphur dioxide emissions of 24 000 t d^{-1} (one of the highest rates recorded), and HCl emissions of *ca*. 10 000 t d^{-1} inferred from the measured plume S:Cl ratio of *ca*. 1.2 (Rose *et al*. 1988). Emission rates in July, when the volcano was in a post-eruptive fuming state, were 380 t d^{-1} SO_2 and 8000 t d^{-1} HCl, and declined exponentially subsequently. The total erupted volume was 0.3–0.4 km^3, equivalent to about 0.2 km^3 of dense rock equivalent (DRE) magma.

The high HCl content of the Augustine gases was confirmed by direct sampling of high-temperature fumaroles (870 °C) on the dome in August 1987 (Symonds *et al*. 1990, 1992) (table 1 and figure 4). As at Mt St Helens, S was probably originally released from the magma dominantly as H_2S, with the oxygen fugacity near the NNO. Symonds *et al*. (1990) reported that the Augustine gas samples had the highest HCl

Table 1. *Examples of gas composition data*

(Examples of gas composition data (in mole %) from some andesitic volcanoes mentioned in the text: 'improved' compositions of selected high-temperature fumarole gases from Mt St Helens (Gerlach & Casadevall 1986); reconstructed compositions for high-temperature fumarole gases from Mount St Augustine (Symonds *et al.* 1990); examples of wet gas analyses for Galeras presented by Alfaro & Zapata (1997); data from Nevado del Ruiz by Giggenbach *et al.* (1990); representative unrestored fumarole gas compositions from Unzen volcano (Ohba *et al.* 1994); data for Soufrière Hills estimated by recalculating volcanic gas constituents from Hammouya *et al.* (1998). Comparison of gas data from different volcanoes and compilation of this kind of table is difficult as data are reported in different ways by different authors, and because direct sampling rarely provides consistent results.)

volcano	sample	date	H_2O	H_2	CO_2	CO	SO_2	H_2S	S_2	HCl	HF
Mt St Helens	800925-710	25.09.80	91.58	0.854	6.942	0.06	0.209	0.355	0.0039	—	—
Mt St Helens	CNRS	16.09.81	98.52	0.269	0.913	0.001	0.073	0.137	0.0003	0.089	—
Mt St Helens	CNR	17.09.81	98.6	0.39	0.886	0.002	0.067	0.099	0.0002	0.076	0.03
Mount St Augustine	Dome 2	28.08.87	84.77	0.54	2.27	0.016	6.18	0.68	0.12	5.34	0.086
Mount St Augustine	Dome 3	28.08.87	83.91	0.63	2.40	0.020	5.72	1.00	0.20	6.04	0.086
Galeras	Calvache (88 °C)	08.08.90	93.96	—	3.80	—	1.53	0.70	—	0.02	—
Galeras	Deformes (243 °C)	05.08.90	93.39	—	3.67	—	1.81	0.95	—	0.18	—
Galeras	Deformes (265 °C)	23.11.90	91.34	—	5.22	—	2.08	0.76	—	0.61	—
Galeras	Besolima (514 °C)	05.03.91	83.76	—	9.64	—	5.34	—	—	0.23	—
Nevado del Ruiz	ER	24.09.85	95.5	0.009	2.34	—	1.98	0.176	—	0.006	—
Nevado del Ruiz	RI	19.10.85	96.8	0.021	1.69	—	1.235	0.09	—	0.12	—
Nevado del Ruiz	A	12.11.85	96.8	—	2.21	—	0.44	0.48	—	0.009	—
Nevado del Ruiz	B	12.11.85	92.4	—	5.13	—	0.45	1.97	—	0.005	—
Unzen volcano	1 (818 °C)	12.05.92	95.50	0.77	2.70	0.027	0.44	0.24[a]		0.26[b]	
Unzen volcano	3 (801 °C)	21.07.92	96.8	0.645	1.51	0.016	0.45	0.21[a]		0.26[b]	
Unzen volcano	7 (778 °C)	15.02.93	96.4	0.58	2.05	0.023	0.45	0.17[a]		0.29[b]	
Soufrière Hills	lava dome gas	27.02.96	90.3	0.905	4.27	0.014	0.836[c]			3.675	—

Notes: —, species not reported; [a] $H_2S + S_2$ reported; [b] HCl + HF reported; [c] all S as SO_2.

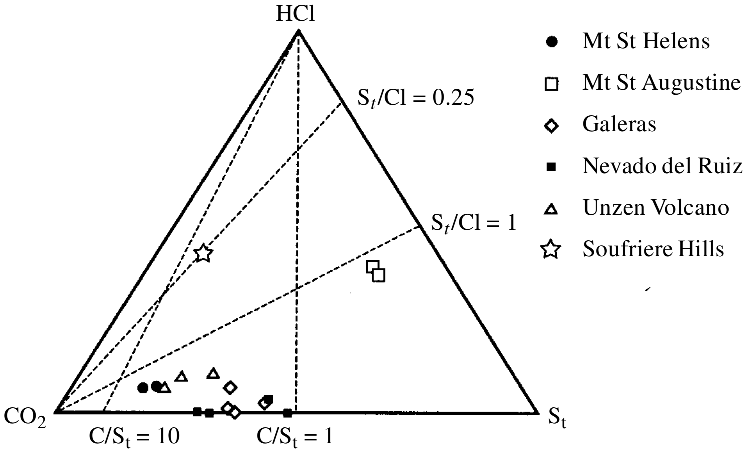

Figure 4. Data from table 1 plotted in the system $HCl–CO_2–S_t$ (where S_t is the total amount of S present as $SO_2 + H_2S + S_2$). Magmatic gases from andesite volcanoes are generally characterized by both C/S and S/Cl ratios in the range of 1–10; a more scattered distribution of data points would be shown were the figure to include more gas data from post-eruptive or quiescent phases where compositions are affected by greater hydrothermal or meteoric input and ratios can fall outside the expected ranges. The Cl-rich nature of gases from Montserrat and Augustine during eruptive episodes is likely related to exceptionally Cl-rich sources (see text).

concentrations ever recorded, and also concluded that they were relatively H_2O and CO_2 depleted. They used hydrogen and oxygen isotope data to infer that the H_2O in the dome gases was a mixture of primary magmatic water and local seawater, and proposed that interactions between seawater and magma at shallow levels (less than 3 km) might account for some of the Cl enrichment in the Augustine gases. However, as argued by Anderson (1975) and demonstrated petrologically by Johnston (1978) on glass inclusions, seawater trapped in subducted oceanic crust provides a source of Cl enrichment in parent magmas.

(*c*) *Redoubt, Alaska: accumulated magmatic vapour,* HCl *scavenging*

During the December 1989 to January 1990 episode of dome extrusion and explosive activity at Redoubt, Hobbs *et al.* (1991) used a well-equipped research aircraft to sample gases and particles in the plume. Instrumentation included a lidar system to obtain range-resolved particle backscatter data, and COSPEC to derive SO_2 emission rates. During intra-eruptive episodes they found that while SO_2 emissions reached *ca.* 8000 t d^{-1}, SO_2:HCl ratios were extremely high (more than 50), with HCl sometimes below detection limits.

Gerlach *et al.* (1994) combined these data with work on volatile contents of melt inclusions to assess the degassing budget of S and Cl. They estimated that whereas TOMS and COSPEC data indicated a total mass of degassed SO_2 of *ca.* 1 000 000 t, petrological estimates yielded only 39 000 t from the *ca.* 0.1 km^3 (DRE) of erupted andesite lava. They concluded that almost all the sulphur in the SO_2 emissions was present as accumulated magmatic vapour at 6–10 km depth; constituting about 0.2 wt% of the magma (*ca.* 0.7 vol.% at depth). They also concluded that CO_2 constituted *ca.* 0.6 wt% of the parent magma, and that this was a key factor in creating the volatile saturation which permitted a vapour phase source of excess S. Citing the implied large volumes and degassing rates of SO_2, they discounted the possibility that gases could have been emitted from unerupted magma beneath the volcano. Given the relatively high Cl concentrations in both phenocryst and matrix glasses, they concluded that the very low measured HCl concentrations in the plume were due to selective scavenging by water vapour.

(*d*) *Mt Spurr, Alaska:* SO_2 *scrubbing*

Routine airborne COSPEC measurements were made throughout the 1991 and 1992 period of unrest at Mt Spurr, which included three explosive events. Only background to minor non-eruptive SO_2 emissions were recorded throughout the entire pre-eruptive period, with the SO_2 emission rate peaking at 750 t d^{-1} on 29 September almost two weeks *after* the third eruption. In contrast, TOMS measurements indicated large eruptive SO_2 emissions for the explosive events themselves: an integrated total of 830 000 t. Doukas & Gerlach (1995) argued that the great difference between non-eruptive and eruptive degassing was due to the role of liquid water in the system. Non-eruptive SO_2 could be easily hydrolysed to aqueous H_2S and sulphate as it passed through the near surface hydrothermal system (a crater lake was present right up to the onset of the first eruption). During explosive events andesite magma ascended rapidly to the surface and could degas directly to the atmosphere, preventing scrubbing of SO_2 by water. Doukas & Gerlach also proposed that the very large amounts of eruptive SO_2 were sourced both from direct magma degassing, and from boiling of water in the hydrothermal system to release previously hydrolysed non-eruptive SO_2. By the end of the third explosive eruption, the hydrothermal system was inferred to have almost dried out completely, permitting non-eruptive SO_2 emissions to peak on 29 September.

CO_2 emission measurements by MIRAN were commenced on 25 September. They detected a high non-eruptive emission of CO_2 of 11 000 t d^{-1}, despite SO_2 still at only 300 t d^{-1} (Doukas & Gerlach 1995). In such circumstances, CO_2 emission rate measurements are likely to be better guides to the level of magmatic activity than SO_2, because CO_2 is relatively more inert and less susceptible to scrubbing.

(*e*) *Galeras, Colombia: pre-eruptive gas loss, sealing of volcanic system*

During 1989–1990 up to 5000 t d^{-1} of SO_2 were emitted from Galeras. This period of strong degassing was followed by emplacement of an andesitic lava dome, and a gradual decrease in SO_2 emission rate. An explosion in July 1992 destroyed the dome, and further Vulcanian eruptions followed in 1993. Stix *et al.* (1993) found that while sulphur concentrations in both glass inclusions and matrix glasses were extremely low (less than 100 ppm), chlorine concentrations were much higher in glass inclusions (1830–2690 ppm) than in matrix glasses (mean 760 ± 270 ppm). They inferred that the magma had degassed to a significant degree before dome extrusion, and that the originally high S:Cl magma had lost significant sulphur before glass inclusion entrapment.

Fischer *et al.* (1994) noted that the amplitude and duration of long-period earthquakes first increased and then decreased over the month before the 23 March eruption. Over the same period, SO_2 emissions declined to extremely low levels, but increased sharply after the eruption. They attributed this to sealing of the system by clays and hydrothermal minerals resulting from alteration of the edifice by acid gases. This increased the pressure in the uppermost, altered parts of the volcano but decreased the pressure gradient between the alteration zone and magmatic source region.

For the period 1988–1993, Fischer *et al.* (1996) showed that the mid- to low-temperature fumarole gases (200–400 °C) were relatively depleted in HCl. They proposed that interaction of magmatic gases with the hydrothermal system is related to the extent to which the carapace enclosing the system is sealed by alteration processes. During times of relatively open-system magmatic degassing, gas compositions are S_t+HCl dominated, and SO_2 emission rates are low, whereas during periods of hydrothermal interaction, variations in composition and the SO_2 emission rate are both greater. On the basis of the inert gas (N_2, Ar and He) content of their samples, Fischer *et al.* (1997) were able to identify the influence of a fresh basaltic intrusion at depth (more than 4 km) on the fumarole compositions during 1993, the year of increased eruptive activity.

(*f*) *Nevado del Ruiz, Colombia: gas released from crystallizing magma*

The 13 November 1985 eruption of Nevado del Ruiz followed a period of about a year of increases in felt seismicity and emission of gases from the Arenas crater. Only 3.5×10^6 t of andesitic pyroclastic rocks were ejected by the eruption, whereas satellite-borne TOMS sensors detected *ca.* 6.6×10^5 t of sulphur dioxide gas (Williams *et al.* 1990). Fumarole samples were collected before and after the eruption, the last sample being collected the day before. According to Williams *et al.* (1986), fumarole composition became less water rich immediately before the eruption, while the S:Cl ratio increased. Giggenbach *et al.* (1990) argued that the pre-eruption gases were anomalously S-rich relative to other volcanoes, and that HCl may have been selectively removed in the hydrothermal system. Williams *et al.* calculated that a total of 3.4×10^6 t of sulphur dioxide was emitted during the four-year period after the eruption, at a rate of 1–2000 t d^{-1}, and concluded that this high level of sustained degassing could only be supplied by a large volume of crystallizing magma.

(*g*) *Unzen, Japan:* SO_2 *emission correlates with magma extrusion, remote measurements of* HCl

Extrusion of an andestic/dacitic lava dome at Unzen began in May 1991, and continued for three years (Nakada *et al.* 1995). Overall, the rate of SO_2 emission was relatively low during the eruption (*ca.* 200 t d^{-1}), but increased after the June explosions (Hirabayashi *et al.* 1995). Lava was extruded at a rate of 3.4 $m^3\ s^{-1}$ until the end of 1991, when it declined to 2.1 $m^3\ s^{-1}$ in March 1992 and then to 1.4 $m^3\ s^{-1}$ in July 1992. Hirabayashi *et al.* (1995) showed that the emission rate of SO_2 correlated loosely with the magma extrusion rate over the three years of observation, with 130–150 g of sulphur being degassed per ton of erupted magma. Sulphur concentrations in plagioclase melt inclusions were low (*ca.* 30 ppm). They concluded that a high-temperature mafic magma was the source of the degassed sulphur.

During 1992, Mori *et al.* (1993) used OP-FTIR spectroscopy to make the first remote measurements of HCl in volcanic gases. They found that the SO_2:HCl ratio lay in the range 0.7–1.8 during the period of observation. Ohba *et al.* (1994) collected high-temperature fumarole gas samples (720–818 °C) on four occasions and measured

SO_2:HCl ratios in the range 1.57–2.54, generally higher than those reported by Mori *et al*. over a similar period.

(*h*) *Soufrière Hills, Montserrat: accumulated magmatic vapour, temporal variation in gas composition*

Since the inception of the eruption in 1995, COSPEC observations have indicated a progressive increase in 'background' SO_2 emission rate through time, broadly coincident with the accelerating rate of magma extrusion. SO_2 emission rate has proved to be a useful proxy measurement for magma production rate (Young *et al*. 1998). Significant increases in emission rate were identified in association with early phreatic eruptions (800 t d^{-1}); episodes of dome collapse and pyroclastic flow generation (900–1500 t d^{-1}); and periods of accelerated dome growth (500–600 t d^{-1}). Observed SO_2 emission rates are about twice those inferred from analyses of glass inclusions in phenocrysts, implying the existence of a S-rich magmatic vapour phase (Barclay *et al*. 1998). Significantly, SO_2 emission did not decline when dome growth ceased in 1998, but continued at higher levels than during the early phases of lava extrusion. During a period of intense activity in June 1997, COSPEC measurements indicated that the SO_2 emission rate correlated with the amplitude of tilt cycles, with peaks at maximum deformation gradients (Watson *et al*. 2000).

Filter pack studies made during the early stages of dome growth in March 1996 (Montserrat Volcano Observatory, personal communication) showed low but variable SO_2:HCl ratios, with the lowest values (less than 0.02) being recorded nearest the dome (figure 4). Selective scavenging of HCl may account for the rapid downwind changes in SO_2:HCl ratios. Hammouya *et al*. (1998) confirmed the low SO_2:HCl ratio in direct samples of high-temperature dome fumaroles in February 1996. Intermittent OP-FTIR observations provide the only available measurements of gas ratios for the volcano's summit emissions after 1996 (Oppenheimer *et al*. 2001). They indicate a secular change in the HCl/SO_2 molar ratio from not less than 5 in 1996 to less than 0.5 in 1999. The long-term decrease in HCl/SO_2 ratio accompanied by the overall increase in SO_2 emission rate is consistent with a transition from degassing of silicic to basaltic magma.

4. Some implications for monitoring andesite volcanoes

Monitoring of volcanic gases has been undertaken for decades. Coupled with seismic data, COSPEC measurements of SO_2 emissions have often provided the first indications of impending major eruptions, and have thus played an invaluable role. Recognizing the onset of an eruption, however, is relatively straightforward. But andesite eruptions often last many years, punctuated by occasional crises, and the most hazardous events may occur well after the onset of activity. Forecasting the onset and nature of such developments presents formidable challenges. In many cases, monitoring of volcanic gases is initiated only after activity is well established, and is then continued on an ad hoc and intermittent basis. While the funding and logistical reasons for ad hoc campaigns are readily understandable, from a hazard mitigation perspective they may be of limited value. Usually, they contribute retrospectively to understanding the events that took place, rather than prospectively towards forecasting future trends.

Comparison of the Cook Inlet volcanoes (Augustine, Redoubt and Spurr) shows that gas compositions and emission rates from one volcano to the next along an arc differ according to the specific combination of volatile sources, hydrothermal systems and style of activity. Even at a single volcano, chemical signals vary as the system develops from open to closed with respect to surrounding hydrothermal or meteoric input. It follows that there is no simple general model for volcano degassing: each volcano, and each eruption, presents separate problems. It can be difficult to apply the lessons learned at one volcano to an adjacent one. To understand the role of degassing at a given volcano, either for hazard mitigation or for purely scientific motives, consistent observations sustained over the duration of the activity are essential.

While direct sampling methods have important scientific applications, safety considerations dictate that they are not useful during crisis phases of eruptions. Remote methods of monitoring are essential. COSPEC measurement of SO_2 emissions has been, and remains, the simplest remote method. But although relatively easy to measure, sulphur dioxide emission rate is not always a good proxy for 'eruptive activity' due to its susceptibility to scrubbing in hydrothermal systems. Its relatively low solubility in magmas makes carbon dioxide the first phase to exsolve, thereby allowing partitioning of other volatiles into an early vapour phase. As a signal of magmatic degassing, carbon dioxide emission rates are more reliable than sulphur dioxide as it is relatively more inert in hydrothermal systems.

(*a*) *Future directions*

Several new and existing technologies promise to contribute substantially towards improved volcano monitoring: developments of new instruments for gas measurements are currently very desirable. Automated continuous sensors for individual gases represent the simplest technique, and eliminate many of the hazards of direct sampling. Although such sensors are themselves vulnerable during episodes of intense activity, their costs must be seen in the context of the costs of the monitoring effort as a whole: a single sensor may cost less than the helicopter flight required to place it in position.

Remote methods have obvious advantages in terms of safety. OP-FTIR spectroscopy has enormous potential to provide new data on plume gas compositions. For hazard mitigation, the challenge here is to recognize how changes in, for example, SO_2:HCl ratios can be interpreted in terms of volcanic processes. Sustained gas monitoring of eruptions is required, combined with simultaneous geophysical, geodetic and petrological studies. With the collection of such comprehensive datasets, progress in modelling is key in order to establish links between subsurface processes and surface observations: there is much scope to link observed gas data with theoretical and experimental petrology to provide generic models. One further goal will be to distinguish changes in composition due to processes taking place within the plume, which may overprint the volcanic signal. As the work on Popocatapetl by Love *et al.* (1998) demonstrates, changes in SO_2:SiF_4 ratios, marking temperature variations, can be readily detected by OP-FTIR spectroscopy at considerable ranges, and may provide a powerful new means for forecasting eruptions. Many further observations are needed, however, to confirm the widespread utility of this relationship, and to better understand the underlying processes.

While techniques such as OP-FTIR promise to deliver a wealth of improved data on plume gas compositions, measurement of gas emission rates still presents formidable problems. Currently, estimates of emission rates all depend on COSPEC measurements of SO_2 plume cross-sections, coupled with wind speed. The potential for satellite-based measurements of both large and small (tropospheric) volcanic SO_2 emissions is likely to have significant future impact. Developments in Doppler radar techniques such as those described by Seyfried & Hort (1999) show that it is possible to measure plume exit velocities, and thus gas fluxes, directly. While this may have useful applications, especially for studies of plume dynamics, it may be difficult to monitor modestly degassing, pre-eruptive volcanoes.

For the reasons outlined earlier, CO_2 is potentially the most useful gas for volcano monitoring, but measurement of CO_2 emission rates and CO_2:SO_2 ratios present enormous challenges to volcanic gas studies because of the high ambient concentration of CO_2. Within a few hundred metres of the source vent, CO_2 concentrations have declined to a few ppm above background, a particularly difficult problem for instruments using solar radiation subject to absorptions across the whole thickness of the atmosphere. Williams & Dick (1995) have attempted to address this by developing a prototype GASPEC instrument, which combines aspects of both COSPEC and infrared spectroscopy. Initial results on plumes from electricity generating stations have been encouraging, although the background problem persists and much further development is required.

References

Alfaro, C. M. & Zapata, J. A. 1997 Acid gas emissions from Galeras volcano, Columbia 1989–1994. *J. Volcanol. Geotherm. Res.* **77**, 209–228.

Anderson, A. T. 1975 Some basaltic and andesitic gases. *Rev. Geophys. Space Phys.* **13**, 37–55.

Barclay, J., Rutherford, M. J., Carroll, M. R., Murphy, M. D., Devine, J. D., Gardner, J. & Sparks, R. S. J. 1998 Experimental phase equilibria constraints on pre-eruptive storage conditions of the Soufrière Hills magma. *Geophys. Res. Lett.* **25**, 3437–3440.

Bluth, G. J. S., Schnetzler, C. C., Kreuger, A. J. & Walter, L. S. 1993 The contribution of explosive volcanism to global atmospheric sulphur dioxide concentrations. *Nature* **366**, 327–329.

Brown, L. R., Farmer, C. B., Rinsland, C. P. & Zander, R. 1992 Remote sensing of the atmosphere by high resolution infrared absorption spectroscopy. In *Spectroscopy of the Earth's atmosphere and interstellar medium* (ed. K. Nahari Rao & A. Weber), pp. 97–151. Academic.

Burton, M. R., Oppenheimer, C., Horrocks, L. A. & Francis, P. W. 2000*a* Diurnal changes in volcanic plume chemistry observed by lunar and solar occultation spectroscopy. *Geophys. Res. Lett.* (Submitted.)

Burton, M. R., Oppenheimer, C., Horrocks, L. A. & Francis, P. W. 2000*b* Field measurement of CO_2 and H_2O emissions from Masaya Volcano, Nicaragua, by Fourier transform spectroscopy. *Geology.* (Submitted.)

Casadevall, T. J., Johnson, D. A., Harris, D. M., Rose, W. I., Malinconico, L. L., Stoiber, R. E., Bornhorst, T. J., Williams, S. N., Woodruff, L. & Thompson, J. M. 1981 SO_2 emission rates at Mount St Helens from March 29 through December, 1980. In *The 1980 eruptions of Mt St Helens, Washington* (ed. P. W. Lipman & D. R. Mullineaux). *USGS Prof. Paper* **1250**, 193–200.

Casadevall, T. J., Rose, W. I., Gerlach, T. J., Greenland, L. P., Ewert, J., Wunderman, R. & Symonds, R. 1983 Gas emissions and the eruptions of Mt St Helens through 1982. *Science* **221**, 1383–1385.

Daag, A. S. (and 9 others) 1996 Monitoring sulfur dioxide emissions at Mt. Pinatubo. In *Fire and mud: eruptions and lahars of Mt Pinatubo, Philippines* (ed. C. G. Newhall & R. S. Punongbayan), pp. 409–414. Seattle: University of Washington Press.

Doukas, M. P. & Gerlach, T. M. 1995 Sulfur dioxide scrubbing during the 1992 eruption of Crater Peak, Mount Spurr volcano, Alaska. In *The 1992 eruptions of Crater Peak vent, Mount Spurr volcano, Alaska* (ed. T. E. C. Keith). USGS Bulletin B-2139, pp. 47–57.

Fischer, T. P., Morrisey, M. M., Calvache, M. L., Diego Gomez, M., Torres, R. C., Stix, J. & Willliams, S. N. 1994 Correlations between SO_2 flux and long period seismicity at Galeras volcano. *Nature* **368**, 135–137.

Fischer, T. P., Arehart, G. B., Sturchio, N. C. & Williams, S. N. 1996 The relationship between fumarole gas compositions and eruptive activity at Galeras volcano, Colombia. *Geology* **24**, 531–534.

Fischer, T. P., Sturchio, N. C., Stix, J., Arehart, G. B., Counce, D. & Williams, S. N. 1997 The chemical and isotopic composition of fumarolic gases and spring discharges from Galeras volcano, Colombia. *J. Volcanol. Geotherm. Res.* **77**, 229–253.

Francis, P. W., Maciejewski, A., Oppenheimer, C. M. M., Chaffin, C. & Caltabiano, T. 1995 SO_2:HCl ratios in the plumes of Mt Etna and Vulcano determined by Fourier transform spectroscopy. *Geophys. Res. Lett.* **22**, 1717–1720.

Francis, P. W., Chaffin, C., Maciejewski, A. J. H. & Oppenheimer, C. M. M. 1996 Remote determination of SiF_4 in volcanic plumes: a new tool for volcano monitoring. *Geophys. Res. Lett.* **23**, 249–252.

Francis, P. W., Burton, M. & Oppenheimer, C. M. M. 1998 Remote measurements of volcanic gas compositions by solar occultation spectroscopy. *Nature* **396**, 567–570.

Gerlach, T. M. 1993 Thermodynamic evaluation and restoration of volcanic gas analyses: an example based on modern collection and analytical methods. *Geochem. J.* **27**, 305–322.

Gerlach, T. M. & Casadevall, T. J. 1986 Fumarole emissions at Mt. St Helens volcano, June 1980 to October 1981: degassing of a magma-hydrothermal system. *J. Volcanol. Geotherm. Res.* **28**, 141–160.

Gerlach, T. M. & McGee, K. A. 1994 Total sulfur dioxide emissions and pre-eruption vapor-saturated magma at Mt. St Helens, 1980–88. *Geophys. Res. Lett.* **21**, 2833–2836.

Gerlach, T. M., Westrich, H. R., Casadevall, T. J. & Finnegan, D. L. 1994 Vapor saturation and accumulation in magmas of the 1989–1990 eruption of Redoubt volcano, Alaska. *J. Volcanol. Geotherm. Res.* **62**, 317–337.

Gerlach, T. M., Delgado, H., McGee, K. A., Doukas, M. P., Venegas, J. J. & Cardenas, L. 1997 Application of the LI-COR CO_2 analyzer to volcanic plumes: a case study, volcan Popocatapetl, Mexico, June 7 and 10, 1995. *J. Geophys. Res.* B **102**, 8005–8019.

Gerlach, T. M., McGee, K. A., Sutton, A. J. & Elias, T. 1998 Rates of volcanic CO_2 degassing from airborne determinations of SO_2 emission rates and plume CO_2/SO_2: test study at Pu'u O'o cone, Kilauea volcano, Hawaii. *Geophys. Res. Lett.* **25**, 2675–2678.

Giggenbach, W. F., Garcia, N., London, A., Rodriguez, L., Rojas, N. & Calvache, M. L. 1990 The chemistry of fumarolic vapor and thermal-spring discharges from the Nevado del Ruiz volcanic–magmatic–hydrothermal system, Colombia. *J. Volcanol Geotherm. Res.* **42**, 13–39.

Hammouya, G., Allard, P., Jean-Baptiste, P., Parello, F., Semet, M. P. & Young, S. R. 1998 Pre- and syn-eruptive geochemistry of volcanic gases from Soufrière Hills of Montserrat, West Indies. *Geophys. Res. Lett.* **25**, 3685–3688.

Harris, D. M. & Rose, W. I. 1996 Dynamics of carbon dioxide emissions, crystallization, and magma ascent: hypotheses, theory, and applications to volcano monitoring at Mount St Helens. *Bull. Volcanol.* **58**, 163–174.

Hirabayashi, J., Ohba, T., Nogami, K. & Yoshida, M. 1995 Discharge rate of SO_2 from Unzen volcano, Kyushu, Japan. *Geophys. Res. Lett.* **22**, 1709–1712.

Hobbs, P. V., Radke, L. F., Lyons, J. H., Ferek, R. J. & Coffman, D. J. 1991 Airborne measurements of particle and gas emissions from the 1990 volcanic eruptions of Mount Redoubt. *J. Geophys. Res.* D **96**, 18 735–18 752.

Johnston, D. 1978 Volatiles, magma mixing and explosive mechanism of Augustine volcano, Alaska. PhD thesis, University of Washington, Seattle.

Kodosky, L. G., Motyke, R. J. & Symonds, R. B. 1991 Fumarolic emissions from Mt St Augustine, Alaska: 1979–1984 degassing trends, volatile sources and their possible role in eruptive style. *Bull. Volcanol.* **53**, 381–394.

Le Guern, F. 1983 Magmatic gas monitoring. In *Forecasting volcanic events* (ed. H. Tazieff & J. C. Sabroux), pp. 293–310. Elsevier.

Love, S. P., Goff, F., Counce, C., Siebe, C. & Delgado, H. 1998 Passive infrared spectroscopy of the eruption plume at Popocatapetl volcano, Mexico. *Nature* **396**, 563–566.

McGee, K. A. & Sutton, A. J. 1994 Eruptive activity at Mount St Helens, Washington, USA 1984–1988: a gas geochemistry perspective. *Bull. Volcanol.* **56**, 435–446.

Mori, T. & Notsu, K. 1997 Remote CO, COS, CO_2, SO_2, HCl detection and temperature estimation of volcanic gas. *Geophys. Res. Lett.* **24**, 2047–2050.

Mori, T., Notsu, K., Tohjima, Y. & Wakita, H. 1993 Remote detection of HCl and SO_2 in volcanic gas from Unzen volcano, Japan. *Geophys. Res. Lett.* **20**, 1355–1358.

Mori, T., Notsu, K., Tohjima, Y., Wakita, H., Nuccio, P. M. & Italiano, F. 1995 Remote detection of fumarolic gas chemistry at Vulcano, Italy, using an FT-IR spectral radiometer. *Earth Planet Sci. Lett.* **134**, 219–224.

Nakada, S., Motomura, Y. & Shimizu, H. 1995 Manner of magma ascent at Unzen volcano, Japan. *Geophys. Res. Lett.* **22**, 567–570.

Ohba, T., Hirabayashi, J. I. & Yoshida, M. 1994 Equilibrium temperature and redox state of volcanic gas at Unzen volcano, Japan. *J. Volcanol. Geotherm. Res.* **60**, 263–272.

Oppenheimer, C., Francis, P., Burton, M., Maciejewski, A. J. H. & Boardman, L. 1998 Remote measurements of volcanic gases by Fourier transform infrared spectroscopy. *Appl. Phys.* B **67**, 505–515.

Oppenheimer, C., Edmonds, M., Francis, P. & Burton, M. R. 2001 Variation in HCl/SO_2 gas ratios at Soufrière Hills volcano observed by Fourier transform spectroscopy, 1996–1999. *Geol. Soc. Lond.* (Spec. Publ. on Montserrat). (In preparation.)

Punongbayan, R. S., Newhall, C. G., Bautista, Ma. L. P., Garcia, D., Harlow, D. H., Hoblitt, R. P., Sabit, J. P. & Solidum, R. U. 1996 Eruption hazard assessment and warnings. In *Fire and mud: the eruptions and lahars of Mount Pinatubo, Philippines* (ed. C. G. Newhall & R. S. Punongbayan). Seattle: University of Washington Press.

Read, W. G., Froidevaux, L. & Waters, J. W. 1993 Microwave limb sounder measurement of stratospheric SO_2 from Mt Pinatubo volcano. *Geophys Res. Lett.* **20**, 1299–1302.

Realmuto, V. J., Sutton, A. J. & Elias, T. 1997 Multispectral thermal infrared mapping of sulfur dioxide plumes: a case study from the East Rift Zone of Kilauea Volcano, Hawaii. *J. Geophys. Res.* B **102**, 15 057–15 072.

Rose, W. I., Heiken, G., Wohletz, K., Keppler, D., Barr, S., Miller, T., Chuan, R. L. & Symonds, R. B. 1988 Direct rate measurements of eruption plumes at Augustine volcano—a problem of scaling and uncontrolled variables. *J. Geophys. Res.* B **93**, 4485–4499.

Seyfried, R. & Hort, M. 1999 Continuous monitoring of volcano eruption dynamics: a review of various techniques and new results from a frequency modulated radar Doppler system. *Bull. Volcanol.* **60**, 627–639.

Stix, J. (and 10 others) 1993 A model for degassing at Galeras volcano, Colombia, 1988–1993. *Geology* **21**, 963–967.

Stoiber, R. E., Malinconico, L. L. & Williams, S. N. 1983 Use of the correlation spectrometer at volcanoes. In *Forecasting volcanic events* (ed. H. Tazieff & J. C. Sabroux). Elsevier.

Symonds, R. B., Rose, W. I, Gerlach, T. M., Briggs, P. H. & Harmon, R. S. 1990 Evaluation of gases, condensates and SO_2 emissions from Augustine volcano, Alaska: the degassing of a Cl-rich volcanic system. *Bull. Volcanol.* **52**, 355–374.

Symonds, R. B., Reed, M. H. & Rose, W. I. 1992 Origin, speciation and fluxes of trace-element gases at Augustine volcano, Alaska: insights into magma degassing and fumarolic processes. *Geochim. Cosmochim. Acta* **56**, 633–637.

Symonds, R. B., Rose, W. I., Bluth, G. J. S. & Gerlach, T. J. 1994 Volcanic-gas studies: methods, results and applications. *Rev. Mineral.* **30**, 1–66.

Watson, I. M., Oppenheimer, C., Voight, B., Francis, P. W. (and 12 others) and MVO staff 2000 The relationship between degassing and ground deformation at Soufrière Hills volcano, Montserrat. *J. Volcanol. Geotherm. Res.* (In the press.)

Williams, S. N. & Dick, R. 1995 Remote measurement of CO_2 in volcanic plumes: first tests on plumes from fossil-fired power plants. *Eos* **76**. Fall Meeting Supplement, F670.

Williams, S. N., Stoiber, R. E., Garcia, N. P., Londono, A., Gemmel, J. B., Lowe, D. R. & Connor, C. B. 1986 Eruption of the Nevada del Ruiz volcano, Colombia, on 13 November, 1985: gas flux and fluid geochemistry. *Science* **233**, 964–967.

Williams, S. N., Sturchio, N. C., Calvache, M. L., Mendez, R., Londono, A. & Garcia, N. 1990 Sulfur dioxide from Nevado del Ruiz volcano, Colombia: total flux and istopic constraints on its origin. *J. Volcanol. Geotherm. Res.* **42**, 153–168.

Williams, S. N., Schaefer, S. J., Calvache, M. L. & Lopez, D. 1992 Global carbon dioxide emission to the atmosphere by volcanoes. *Geochim. Cosmochim. Acta* **56**, 1765–1770.

Young, S. R. (and 12 others) 1998 Monitoring SO_2 emission at the Soufrière Hills volcano: implications for changes in eruptive conditions. *Geophys. Res. Lett.* **25**, 3681–3684.