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Changes in gas composition prior to a minor explosive eruption at Masaya volcano, Nicaragua

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Abstract

A small explosive eruption at Masaya volcano on 23 April 2001, in which a number of people were injured, was preceded by a distinct change in plume gas compositions. Open-path Fourier transform infrared spectroscopy (FTS) measurements show that the SO_2/HCl molar ratio increased from 1.8 to 4.6 between April 2000 and April/May 2001. The SO_2 flux decreased from 11 to 4 kg s^{-1} over this period. We interpret these changes to be the result of scrubbing of water-soluble magmatic gases by a rejuvenated hydrothermal system. A sequence of M 5 earthquakes with epicentres about 7 km from the volcano occurred in July 2000. These may have altered the fracture permeability close to the magmatic conduit, and caused increased magmatic–hydrothermal interaction, leading eventually to the phreatic explosion in 2001. Continuous FTS measurements at suitable volcanoes could provide useful information in support of eruption prediction and forecasting.

Keywords: Fourier transform infrared spectroscopy; volcanic gas; volcano monitoring; Masaya

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1. Introduction

Minor phreatic, phreatomagmatic or magmatic explosive eruptions are difficult to predict, as little is known about potential precursory signals. Although such minor events typically affect only a small area, several cases in recent years have demonstrated that they can pose a considerable risk to sightseers, scientists and others in the vicinity of volcanic vents. Our general aim here is to consider whether such events might have a detectable geochemical precursor.

Studies at several volcanoes have led to models to explain the occurrence of small explosions. For the dome-building eruption of Galeras, Colombia, Stix et al. (1993) suggested that sealing and pres-

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surisation might lead to explosive eruptions. This idea was developed by Fischer et al. (1994) who examined the correlation between gas flux and seismicity at Galeras, finding that the unsteady release of magmatic gases through cracks caused pressure fluctuations associated with long-period seismic events observed in early 1993 (after a fatal eruption in January that year). At Stromboli, Italy, around 3–10 explosions occur per hour (Chouet et al., 1997). Occasional stronger 'paroxysmal' eruptions have resulted in injuries and fatalities amongst tourists, most recently in 2001 (Smithsonian Institution, 2001b). Similar fatal eruptions have also occurred recently at Semeru in Java (Smithsonian Institution, 2000). There has been considerable interest in identification of possible precursors to such events. Chouet et al. (1999) recognised a characteristic compression–dilation–compression sequence in broadband seismograms from Stromboli, which they interpreted as the result of a cyclical process of pressurisation and depressurisation of the conduit associated with the ascent and release of gas. White and Houghton (2000) described the 1976–1982 White Island eruption episode as consisting of alternating Strombolian and phreatomagmatic phases. The phreatomagmatic phases comprised continuous emissions of gas and ash, or discrete large explosions. The large explosions were thought to be triggered by the interaction of magma with brine-saturated wall rocks. These examples represent diverse volcanoes and eruption styles, and with an increasing number of visitors and tourists to volcanoes, they highlight a need to explore methods that may identify the increased likelihood of such small explosive events.

A recent example of this risk is given by Masaya volcano, Nicaragua (Fig. 1), which produced one of its most energetic explosions in about 30 years on 23 April 2001. The eruption lasted for about 2 min, and expelled blocks (up to 60 cm across) over the main car park at the crater rim, along with quantities of ash (Smithsonian Institution, 2001a). It appears to have been phreatic in character as the coarse ejecta were non-vesicular, dense clasts covered in hydrothermal deposits. These blocks were probably old lavas that were excavated to form a new vent, some 10 m in diameter, and about 20–30 m south of the pre-existing vent. Most of the degassing now appears to be focused from this new vent (Fig. 1a,c). Some of the blocks were hot enough to ignite the surrounding dry vegetation (Fig. 1d).

More than 120 tourists were at the crater rim at the time of the explosion, and several sustained minor injuries from impacts with the ejecta and from falls while fleeing the scene. Several vehicles were also damaged. No seismic precursors to the April 2000 eruption were identified (Smithsonian Institution, 2001a). We report here contemporary observations of sulphur, carbon and halogen emissions from Masaya, measured by open-path Fourier transform infrared spectroscopy (FTS) and consider whether observed changes in degassing could be interpreted as a factor in, or indicator of, the eruption. Ultimately, the aim is to establish the relationships between the chemistry and dynamics of degassing that may be used as more general indicators of this kind of activity at volcanoes worldwide.

2. Prior work at Masaya volcano

Masaya (11.984°N, 86.161°W) is a low (560 m above sea level) basaltic shield volcano approximately 25 km southeast of Managua in Nicaragua. It is one of the few volcanoes thought to have produced basaltic Plinian activity (at ~20 and ~6.5 kyr B.P.; Williams, 1983). Gas crises (i.e. periods of strong degassing not associated with a major eruption) lasting years to decades have occurred periodically at Masaya, and the volcano has been in a phase of persistent degassing since 1993. Occasional minor explosions scatter ejecta around the summit area and result in temporary closure of the national park in which it is situated.

FTS measurements of gas emissions have been carried out at several volcanoes, including Unzen (Mori et al., 1993), Mount Etna (Francis et al., 1995; Burton et al., 2003) and Popocatépetl (Love et al., 1998). Stoiber et al. (1986) measured volcanic gases at Masaya by filter pack sampling, and by ultraviolet spectroscopy (using a correlation spectrometer, COSPEC). Rymer et al. (1998)

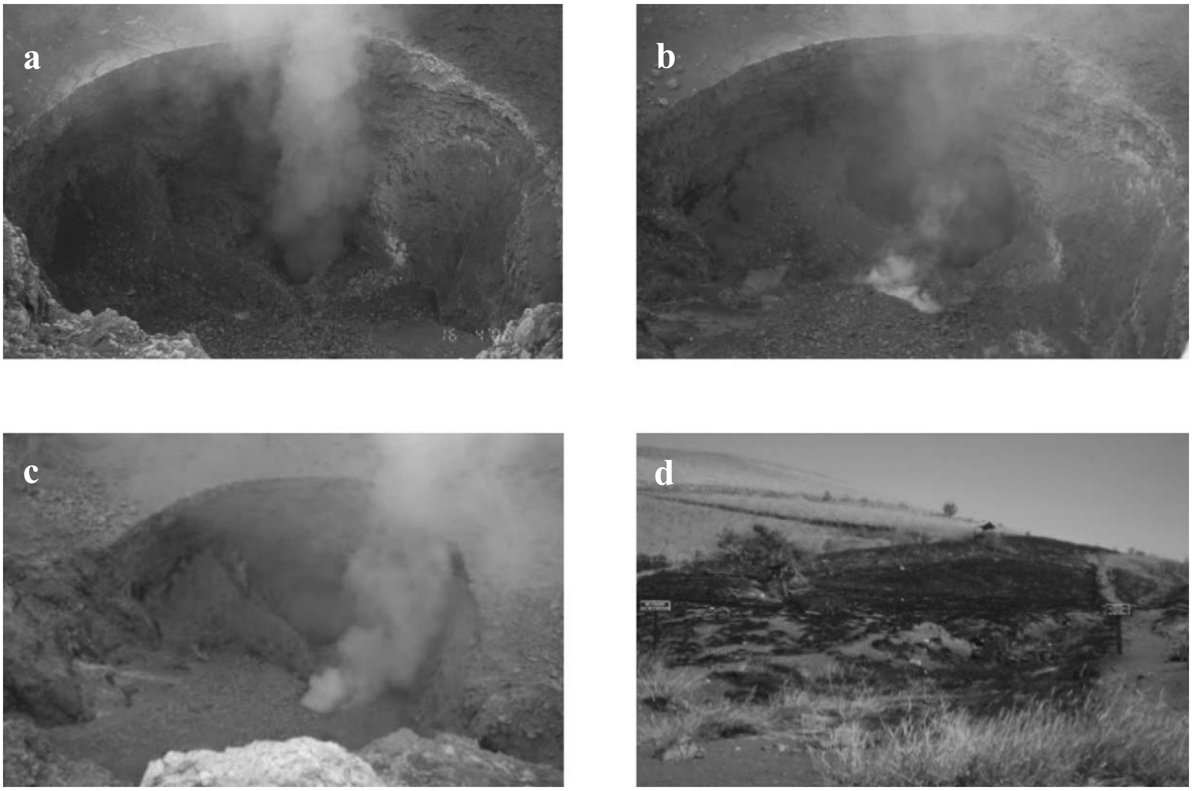

Fig. 1. Photographs of Masaya crater. (a) Degassing from old vent in April 2000, approximate vent diameter 15 m. (b) Fumarolic activity in April 2001, before the explosion. (c) Degassing from new vent, in April 2001, after the explosion. (a), (b) and (c) pictured from SW car park looking NE. (d) Burnt vegetation around crater edge, taken from NE car park looking east.

explained pit crater formation at Masaya through collapse along outward-dipping faults and unroofing of small chambers. From gas and microgravity measurements they proposed a model of periodic convective overturn of the magma. Based on gas chemistry and flux observations using both FTS and COSPEC, Horrocks et al. (1999), Horrocks (2001) and Delmelle et al. (1999) suggested that shallow, open-system degassing in the conduit feeding Masaya's Santiago crater drives convection, enabling large quantities of volatile-rich magma to lose gas efficiently without vigorous eruption, a conclusion similar to that reached by Francis et al. (1993). From seismic analyses, Métaxian et al. (1997) have also proposed an open magmatic system, with the permanent tremor at Masaya generated by the continuous degassing from a lava lake, or a shallow magma body when a lake is not present.

FTS campaigns at Masaya volcano began in 1998 (Horrocks et al., 1999) and have taken place each year, sometimes combined with other monitoring techniques at the volcano (Delmelle et al., 1999, 2001). Burton et al. (2001) used the Moon as an infrared source to make gas-phase measurements at night, and revealed greater SO_2/HCl ratios than those derived from daytime measurements using the Sun. They proposed this to be due to the dissolution of HCl into water droplets in the strongly condensed plume at night. Burton et al. (2000) calculated CO_2 and H_2O fluxes, while Duffell et al. (2001) used solar occultation to determine fluxes of several species (SO_2, HCl, HF, CO_2 and H_2O) by making traverses beneath the plume with the FTIR spectrometer optically joined to a dynamic Sun-tracker.

The discontinuous measurement periods of February–March 1998, March 1999, April 2000

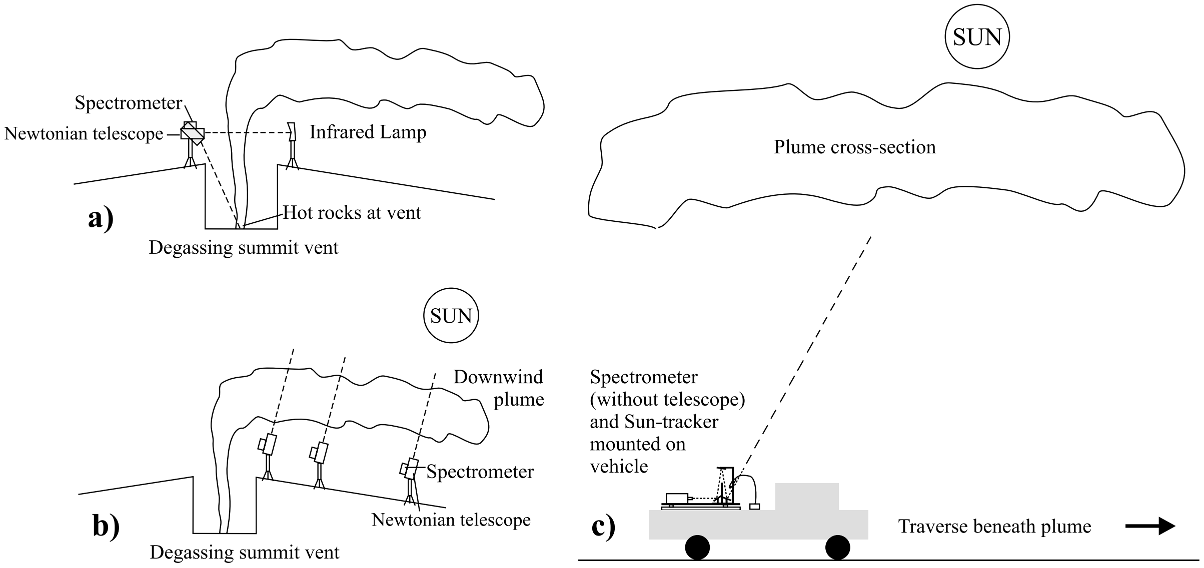

Fig. 2. Diagrams showing modes of FTS deployment. (a) and (b) are from Oppenheimer et al. (1998). (a) Infrared lamp or hot rocks used as source over a specified pathlength. (b) Sun used as infrared source. Both the lamp and Sun can be used as IR sources at the summit or at different distances downwind from the volcano. A Newtonian telescope is used to collimate the light into the spectrometer. (c) Sun used as infrared source and a Sun-tracker allows cross-sectional traverses beneath the plume. This can also be used in a fixed position instead of using the Newtonian telescope.

and April–May 2001 are referred to in this paper as 1998, 1999, 2000 and 2001, respectively. Previous work had shown very similar gas compositions in each of the campaigns in 1998, 1999 and 2000 (Horrocks et al., 1999, 2003).

3. Materials and methods

The measurements reported here were all obtained by FTS. Between 1998 and 2000 our research group used a MIDAC spectrometer equipped with an InSb detector delivering a useful signal between about 5000 and 2000 cm^{-1} at 0.5 cm^{-1} resolution. In 2001, a BOMEM spectrometer was used, with an InSb detector operating at 1.0 cm^{-1} resolution. SO_2, HCl and HF were seen in absorption, and gas column concentrations for these, and atmospheric trace gas species, were determined using the HITRAN96 database (http://www.hitran.com/) with a forward model (Reference Forward Model, version 4.0, http://www.atm.ox.ac.uk/rfm) and a non-linear least-squares algorithm (Rodgers, 1976). Gas species quantified include SO_2, HCl, HF, H_2O, CO_2, CH_4 and N_2O. Several other infrared active gases

Table 1
Spectral ranges for FTS gas retrievals at Masaya

Publication	Spectral windows (cm^{-1})			
	SO_2	HCl	HF active	HF solar[a]
Horrocks et al. (1999)	2465–2550	2690–3040	4000–4200	
Burton et al. (2000)	2450–2550	2690–3040	4030–4200	
Duffell et al. (2001)	2480–2520	2690–2830	4050–4150	4030–4180
this work	2465–2540	2690–2830	4030–4050	4165–4185

[a] Some solar spectra in Duffell et al. (2001) showed no energy in the 4000 cm^{-1} region due to a large water absorption feature, so an optimal HF spectral range was chosen in which all solar HF spectra could be retrieved.

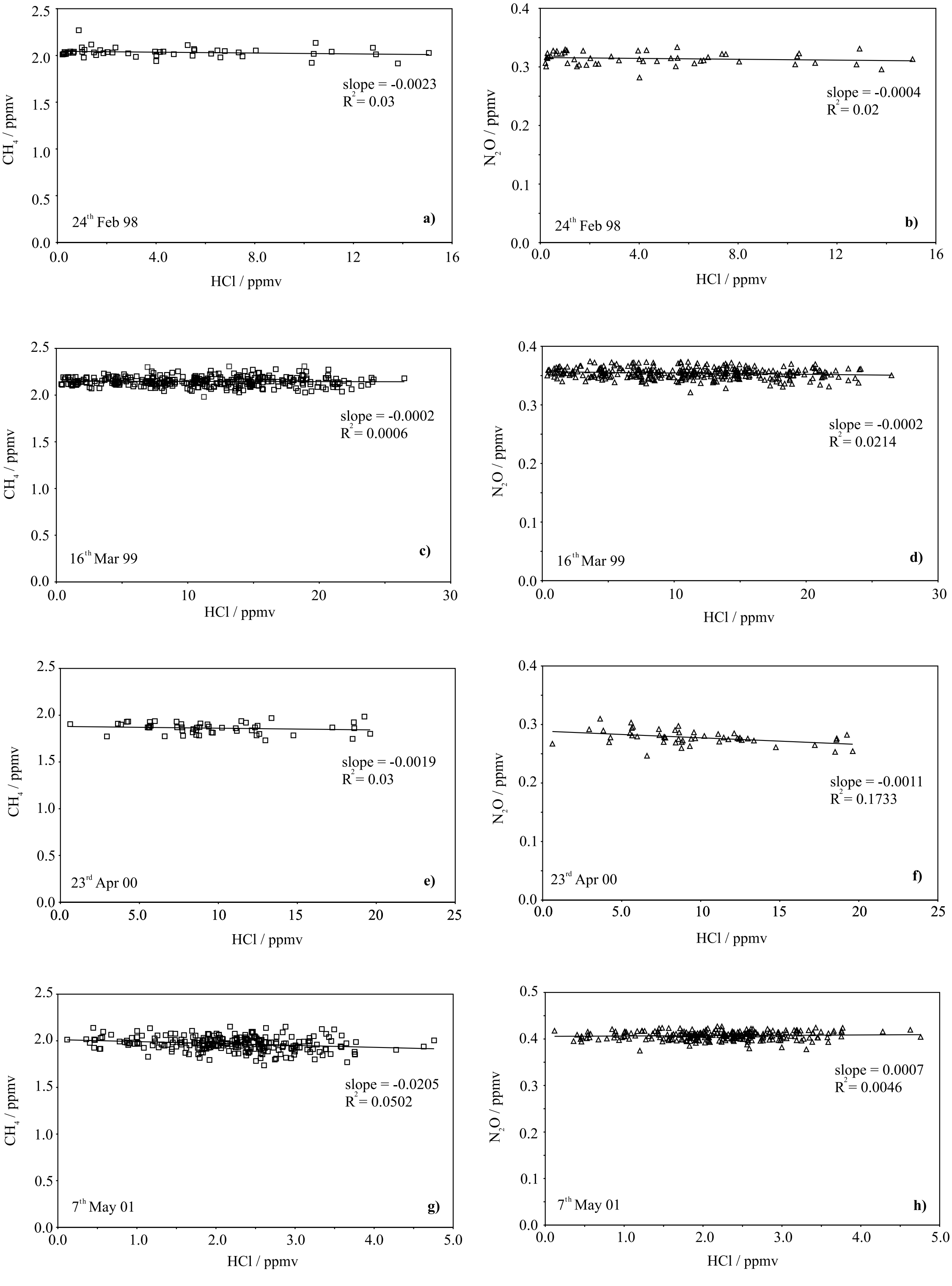

Fig. 3. Representative plots of CH_4 vs. HCl and N_2O vs. HCl for (a) and (b) 24 February 1998; (c) and (d) 16 March 1999; (e) and (f) 23 April 2000; and (g) and (h) 7 May 2001. The linear regression lines give the slope of the data. The lack of correlation between volcanic HCl and the atmospheric gases shows that there is no volcanic component of CH_4 and N_2O.

(such as H_2S) were sought but were not present above detection limits. For an in-depth discussion of the retrieval method, including sensitivity experiments and discussion of errors, see Horrocks et al. (2001).

FTS observations can be made with the equipment in several different configurations (Fig. 2). The infrared source can be an infrared lamp, the Sun or heated rocks (active, solar or passive measurements, respectively), and the equipment can be used at varying distances from the volcanic vent. The infrared lamp measurements were typically taken over a pathlength of ~500 m with the lamp and spectrometer positioned on opposite sides of the crater. Shorter pathlengths at other locations in the volcanic plume may also be used. Solar measurements can be taken at the crater rim and at varying distances downwind with the spectrometer looking directly at the Sun through the plume. Pressure, temperature and relative humidity are logged during data collection using a portable weather station. Pressure and temperature estimates for the plume are required for the retrieval.

Different wavelength ranges or 'microwindows' for spectral fitting have been used to analyse data in different years (Table 1), and this can have an impact on retrieved quantities (Horrocks, 2001). The changes in spectral range from 1999 to 2001 reflect improvements made to the retrieval on the basis of our experience at a number of volcanoes. Although sensitivity experiments on SO_2 retrievals for spectra obtained over a short path with an infrared lamp by Horrocks et al. (2001) indicated an error of only ±1.0% associated with the choice of spectral range and background polynomial, the sensitivity of gas *ratios* of different species to microwindow position and width, and for spectra collected in the field rather than in the laboratory, can be significantly higher. In this paper, we quote published gas ratios for the 1998 and 1999 campaigns (Horrocks et al., 1999; Burton et al., 2000), but we have recalculated ratios for subsets of all data using the same microwindows ('this work' in Table 1) to permit direct comparisons of the results. Although this has a relatively minor impact on the SO_2/HCl ratios (up to 15%), the HCl/HF ratios varied by up to 40% according to choice of spectral range.

3.1. Instrument compatibility

Another factor affecting intercomparison is that we have used two different spectrometers for our measurements, and it is important to verify that the results from the two instruments are compa-

Table 2
Recalculated volume mixing ratios (ppmv) of atmospheric gases at Masaya determined by FTS

Date	CH_4	N_2O
1998		
23 February	1.92 ± 0.03	0.297 ± 0.005
24 February	1.97 ± 0.05	0.30 ± 0.01
25 February	1.96 ± 0.04	0.34 ± 0.01
1999		
09 March	1.9 ± 0.3	0.32 ± 0.06
16 March	2.07 ± 0.05	0.341 ± 0.009
2000		
19 April	1.66 ± 0.07	0.27 ± 0.03
23 April	1.81 ± 0.06	0.27 ± 0.01
24 April	1.71 ± 0.04	0.294 ± 0.007
2001		
17–18 April	1.9 ± 0.1	0.36 ± 0.01
07 May	1.89 ± 0.07	0.391 ± 0.009
08 May	1.72 ± 0.07	0.34 ± 0.01
standard atmospheric concentrations[a]	1.7	0.32

[a] Fegley (1995).

Table 3
Daily molar ratios for gas species determined by FTS, 2001

Date in 2001	SO_2/HCl	HCl/HF	SO_2/HF
12 April	5.0 ± 0.3	8.2 ± 2.4	41 ± 10
17–18 April[a]	4.64 ± 0.01	6.12 ± 0.04	29.6 ± 0.2
21 April	4.51 ± 0.07	9.6 ± 1.2	42.5 ± 5.3
25 April	3.97 ± 0.05	7.9 ± 0.7	30.9 ± 2.9
26 April	3.96 ± 0.06	8.5 ± 1.1	34.1 ± 4.6
27 April	5.8 ± 0.3	–	–
29 April	4.2 ± 0.4	–	–
2 May	4.30 ± 0.04	–	–
3 May	4.16 ± 0.02	–	–
4 May	5.0 ± 0.2	–	–
6 May	4.25 ± 0.04	10.8 ± 0.7	45.7 ± 3.1
7 May[a]	4.06 ± 0.03	8.1 ± 0.2	33.3 ± 0.9
8 May[a]	6.94 ± 0.04	6.7 ± 0.1	46.2 ± 0.9
8 May	4.00 ± 0.02	10.2 ± 0.7	41.6 ± 3.0
9 May	4.0 ± 0.3	–	–

[a] Infrared lamp used as source. Sun used as source for rest of measurements. Ratios and errors calculated using a least-squares fit method.

rable and that the changes in gas ratios are not due to instrumental effects. Although the MIDAC and BOMEM spectrometers have different resolutions (0.5 and 1.0 cm^{-1}, respectively), as long as the instrumental response is well characterised, results should be compatible. Our retrieval algorithm shows the residual for each spectrum (the difference between a simulated atmospheric spectrum and an iterated best fit to the measured spectrum). This provides a first check on instrument compatibility. The residuals were found not to differ substantially from year to year for each gas species being retrieved, suggesting that changes in the results from one year to the next were not due to the different instruments being used. The background concentration of certain atmospheric trace gases such as CH_4 and N_2O cannot have changed significantly during our set of measurements. The non-correlation of both CH_4 and N_2O against HCl, which is exclusively volcanogenic (Fig. 3), confirms that there is no volcanic component for these two atmospheric species. Average volume mixing ratios for CH_4 and N_2O for selected infrared lamp data from 1998 to 2001 are shown in Table 2. These values are from active measurements across the summit crater, and are calculated by dividing the column amounts of gas (ppm m) by the pathlength (m). There is close correspondence of the ambient concentrations of these species, as expected, providing clear evidence for the compatibility of the two spectrometers.

Table 4
Molar ratios determined by FTS for the measurement periods during 1998–2001

Molar ratio	1998[a]	1999[a]	2000	2001[b]
SO_2/HCl	1.57 ± 0.05	1.68 ± 0.05	1.784 ± 0.003	4.589 ± 0.009
HCl/HF	4.5 ± 0.2	4.5 ± 0.2	6.09 ± 0.04	6.17 ± 0.04
SO_2/HF	7.2	7.7	11.06 ± 0.06	29.6 ± 0.2
CO_2/SO_2	2.5 ± 0.2	2.3 ± 0.2	1.5 ± 0.4	2.9 ± 0.2
H_2O/SO_2	69 ± 9	66 ± 10	*62	*30
H_2O/HCl	108.3	110.5	111 ± 6	136 ± 20

[a] Horrocks et al. (1999) and Burton et al. (2000). Data from 2000 and 2001 were calculated using the least-squares fit method as in Table 3, except * are from multiplying ratios together.

[b] Excludes 8 May lamp measurements (see Fig. 4). The 2001 molar ratios for all pre- and all post-eruption (23 April) data (not shown) are: SO_2/HCl 4.7 and 5.0; HCl/HF 6.1 and 8.0; and SO_2/HF 30 and 41.

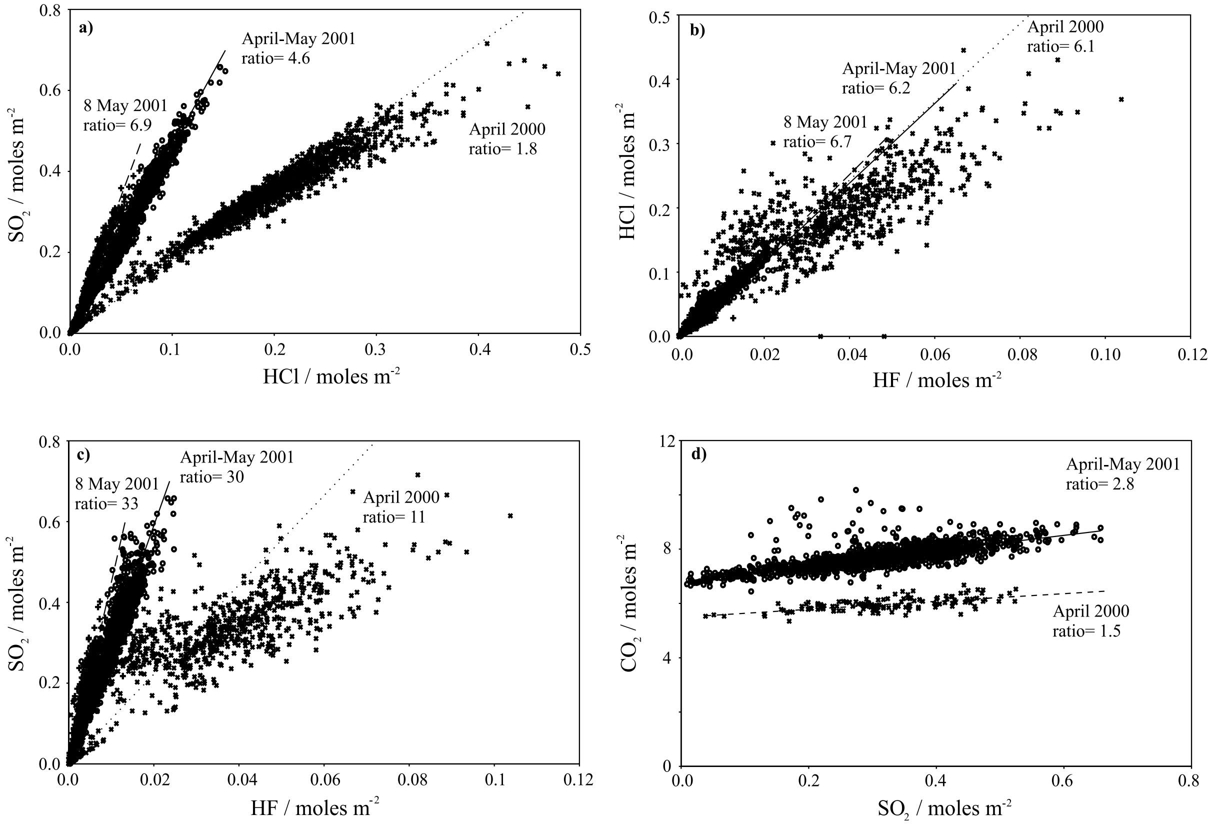

Fig. 4. (a–d) 2000 and 2001 gas column concentrations. x symbols are 2000 data (dotted regression line), circles are 2001 data (solid regression line), and + symbols represent values for 8 May 2001 (dashed regression line). All data retrieved using the same spectral windows (Table 1). Gas ratios calculated from best-fit regressions. (a) SO_2 vs. HCl, (b) HCl vs. HF, (c) SO_2 vs. HF, (d) CO_2 vs. SO_2.

4. Results

Ratios of the halogen and sulphur gas species measured for several days in 2001 are shown in Table 3 (all ratios reported here are molar or volume ratios). Diffusion tubes and filter packs were also deployed at this time but yielded much more variable results, with the SO_2/HCl ratio ranging from 0.5 to 4 (Allen et al., 2002). The gas ratios measured from 1998 to 2001 are shown in Table 4, and the changes in the ratios for the 2000 and 2001 measurement periods are shown in Fig. 4. The SO_2/HCl ratio increased from 1.8 to 4.6 between 2000 and 2001. Over the same period, the HCl/HF ratio stayed constant (6.1 in 2000 and 6.2 in 2001) and consequently the SO_2/HF ratio increased from 11 to 30. The CO_2/SO_2 ratio for 2001 is the highest measured, at 2.84. The high variability seen in the year 2000 HF data probably results from the collection of a large amount of overnight data when plume water contents are high and variable, removing soluble HF from the gas phase. In Fig. 4a–c, some data from 2000 appear far from the regression line as this is controlled by the large number of values that plot near the origin (and are not visible in the graphs due to superposition of other years' data). This clustering of data also results in the small standard deviation in Table 4 for the SO_2/HCl ratios in 2000 and 2001. That the ratios are not as stable as previous years can be seen by the particularly high SO_2/HCl ratio of 6.9 (infrared lamp source) on 8 May 2001, soon after the 23 April eruption.

Table 5 shows a notable decrease in all gas fluxes from 2000 to 2001. Halogen fluxes in 1998 and 1999 were obtained by multiplying FTS-derived sulphur:halogen ratios by contemporaneous COSPEC measurements of the SO_2 flux. Emission rates in 2000 were derived from SO_2 and HCl fluxes measured by FTS traverses beneath the plume (Duffell et al., 2001), and in 2001 from an SO_2 flux measured by differential optical absorption spectrometer (DOAS) traverses (Galle et al., 2002). The SO_2 flux decreased by a factor of 3–5 between 1999 and 2001. Since the SO_2/HCl ratio increased between 2000 and 2001, the HCl decreased by an order of magnitude between 1999 and 2001. While we are duly cautious in interpreting this discontinuous record of data, it clearly hints at a substantial change in the degassing behaviour of Masaya between 2000 and 2001.

Because we only have ratio measurements in April 2000 and April/May 2001, we cannot accurately constrain the timing or rate of change of these parameters. We note that COSPEC measurements of the SO_2 flux in early 2001 (Delmelle, personal communication) and a SO_2 flux from a FTS traverse in April 2000 (Duffell et al., 2001) were already lower than in 1999 (Table 5), however, the emission rate record is limited and the dramatic decrease in 2001 is thought to be more significant.

5. Discussion

The first eruption at Masaya in almost 3 years occurred on 23 April 2001. We observed changes in the gas compositions and fluxes that preceded the eruption. Given that the changes in gas composition and flux occurred prior to this event, we consider whether the change in degassing might have been a factor in the eruption, and hence whether such signals could be deemed precursors. The following observations are considered in the interpretation of the changes in gas composition:

(i) A clear increase (from 1.8 to 4.6) in the SO_2/HCl molar ratio of the volcanic plume between April 2000 and April 2001, prior to the 23 April 2001 explosion. The HCl/HF ratio did not change (Table 4). In 2001, the CO_2/SO_2 ratio was the

Table 5
Gas fluxes from Masaya volcano[a]

Date	Gas flux (kg s^{-1})					Reference[b]
	SO_2	HCl	HF	CO_2	H_2O	
pre-1979 average	4.4					1
January 1980–November 1982	15	9.6	0.19			1
April 1992	0.29					2
March 1996	6.9					2
February–March 1997	4.5					3
February–April 1998	21	7.6	0.9	36	399	3, 4
September 1998	7.8					3
February–March 1999	21	6.9	0.8	34	399	3–5
April 2000	11	3	0.26	11	151	6
January 2001	4.2					7
February 2001	5.6					7
February–March 2001	6.7					8
April 2001	†4	0.5	0.042	7.8	34	this work; †9
December 2001	4					10

[a] SO_2 fluxes are from COSPEC measurements except April 2000 (FTS), April 2001 (DOAS) and December 2001 (DOAS). HCl and HF fluxes are derived from SO_2 flux measurements combined with other gas ratios obtained by FTS (except ref. 1, where filter pack data were used; and ref. 6 where HF, CO_2 and H_2O fluxes were derived from gas ratios combined with a HCl flux measured by FTS traverse).

[b] References: 1 – Stoiber et al., 1986; 2 – Rymer et al., 1998; 3 – Delmelle et al., 1999; 4 – Burton et al., 2000; 5 – Horrocks et al., 1999; 6 – Duffell et al., 2001; 7 – Delmelle, personal communication; 8 – Williams-Jones et al., personal communication; 9 – Galle et al., 2002; 10 – McGonigle et al., 2002.

highest measured (2.84, compared to 1.47 in 2000).

(ii) A factor of 3–5 decrease in the SO_2 flux from 1999 to 2001. The HCl, HF, CO_2 and H_2O fluxes decreased by factors of 14, 19, 4 and 12, respectively, over this same time (Table 5).

(iii) Visual observations of an increase in fumarolic activity and deposition of sulphur adjacent to the vent prior to the explosion (Fig. 1b). The 23 April 2001 vent formed in the location previously occupied by fumaroles.

(iv) In 2001, the incandescence from the vent(s) was considerably weaker than in previous years, suggesting descent of the top of the magma column perhaps by a few metres or tens of metres.

(v) An increased variability in the daily gas chemical ratios compared to previous campaigns was measured after the explosion.

5.1. *Evidence for increased hydrothermal interaction*

While the available data are limited, nonetheless a very clear change in the volcanic gas signature occurred prior to the 23 April 2001 explosion at Masaya. With the poor temporal sampling of the geochemical data and limited supplementary observations (e.g. seismic and geodetic data), interpretations of the observed change in degassing are difficult to constrain. The observed decrease in gas fluxes argues against a fresh input of volatiles into the feeder reservoir, as this would be expected to lead to increased gas fluxes. If a single batch of volatiles were being depleted in the reservoir, the less soluble gases would be expected to have degassed more completely, whereas the observed ratios show an increase in less soluble species, SO_2 and CO_2, with respect to HCl and HF. We believe, therefore, that the change in the gas composition is best explained by the influence of a hydrothermal system.

The potential scrubbing effect of hydrothermal systems on more water-soluble magmatic gas components is well known (e.g. Doukas and Gerlach, 1995; Oppenheimer, 1996). More recently, Symonds et al. (2001) have quantified the potential reactions between magmatic gas, water and country rock. At Masaya, the introduction of water into the system would encourage the dissolution of soluble $HCl_{(g)}$ into the aqueous phase, leading to an increase in the SO_2/HCl gas ratio and a decreased HCl flux as indicated in Table 5. Symonds et al. (2001) showed that sulphur deposition may also occur, limiting the emission of $SO_{2(g)}$. The increase in the CO_2/SO_2 ratio could reflect a degree of SO_2 scavenging. According to Symonds et al. (2001) scavenging may be so efficient that it can be difficult to sustain any SO_2 and HCl gas emissions when liquid water is present in an intervening hydrothermal system. At Masaya, the weak vent glow suggests that there may be some direct degassing of magma at the magma–air interface. We propose that as the magma column dropped, an increased component of gas passing through the conduit walls was intercepted by hydrothermal fluids, reflected in the fumaroles seen close to the original vent prior to the explosion. Gas scrubbing is consistent with the lower observed gas fluxes, particularly for the more water-soluble species. The significantly lower H_2O flux calculated for 2001 (Table 5) supports the presence of $H_2O_{(aq)}$ leading to the scrubbing of H_2O from the gas phase. The phreatic nature of the 2000 explosion is, of course, consistent with increased magma–water (or hot rock–water) interaction.

Several moderate (M 5) seismic events with epicentres at Masaya town (~7 km east of the volcano) occurred in July 2000 (Smithsonian Institution, 2000). Although they had no reported effect on the activity observed at Masaya volcano at the time, part of the crater wall was reported to have collapsed (Smithsonian Institution, 2000). We speculate that these events may have opened up new pathways in the shallow plumbing system, increasing permeability and allowing meteoric water and groundwater to penetrate further into the system resulting in increased hydrothermal activity. It is conceivable, therefore, that these earthquakes played a role in the changed degassing patterns – certainly the timing fits in with the observed gas compositional changes.

5.2. *Post-eruption observations*

Following the explosion on 23 April 2001, the

SO_2/HCl ratio reached a minimum value of around 4, compared to the pre-explosion values of 4.5–5. On 2 days, 27 April and 8 May, the ratio reached 5.7 and 6.9, respectively (Fig. 4a and Table 3). This day to day variability contrasts with prior FTS campaigns at Masaya when the ratios have shown only very slight variations over periods of days to a few weeks (Horrocks et al., 1999, 2003). While we cannot be certain what it is that causes these brief excursions to higher SO_2/HCl ratios, we speculate that they reflect ephemeral hydrothermal processes, and changes in the extent of scrubbing of HCl.

More recent flux measurements confirm that the low SO_2 fluxes, of around 4–6 kg s^{-1}, continued through December 2001 (McGonigle et al., 2002; Table 5).

5.3. SO_2 degassing budget, 1996–2001

From 1996 to 2001 Masaya released around 10^9 kg of sulphur (as S) to the atmosphere. Taking a range of possible values of the sulphur loss per unit mass of melt (from ~100 to ~1500 ppm, Table 6), between 10^{11} and 10^{13} kg of magma has degassed during this period (Table 6). This compares favourably with previous estimates of the amount of magma degassed at Masaya during earlier degassing episodes. For example, Stoiber et al. (1986) calculated that 4.6×10^{12} kg of magma degassed between 1979 and 1985; Rymer et al. (1998) estimated that 1.8×10^{12} kg of magma degassed from 1993 to mid-1997, while, from Delmelle et al. (1999), we calculate that 7.3×10^{11} kg of magma degassed from 1993 to 1999.

The mean magma flux required to supply the SO_2 degassed from 1996 to 2001 is 500–50 000 kg s^{-1}, or 0.2–20 m^3 s^{-1}. Little, or none, of this magma erupted. There is a large uncertainty in these values since the dissolved sulphur content of the magma feeding Masaya's shallow reservoir, and the mass fraction of sulphur degassed, are essentially unknown. Magma fluxes have been estimated at other volcanoes with lava lakes by Harris et al. (1999) based on infrared satellite observations of surface temperature distributions and derived surface heat losses. This is not necessarily representative of the amount of degassed magma, which explains why estimates from Erebus, Pu'u' 'O'o and Erta 'Ale, which range from 30 to 2000 kg s^{-1}, are rather lower than those from Masaya. The imbalance at Masaya between the prodigious release of gas and the minimal extrusion of lava, is consistent with a process of conduit convection that provides a constant supply of volatiles from recycling magma (e.g. Kazahaya et al., 1994; Stevenson and Blake, 1998).

6. Conclusions

Between April 2000 and April 2001, the SO_2/HCl ratio of gases in the plume at Masaya volcano increased by a factor of 3. Previous spectroscopic campaigns at Masaya had indicated a remarkably consistent SO_2/HCl molar ratio of ~1.8 since 1998. By April 2001, this had risen to ~4.6. Between 2000 and 2001 the HCl/HF ratio did not change appreciably, but the CO_2/SO_2 ratio in 2001 (~2.8) was nearly twice the

Table 6
Estimated mass of magma degassed from 1996 to 2001

Sulphur loss on degassing (ppm)	Mass of magma required to yield 9.7×10^8 kg S	Comment
1500	6.45×10^{11} kg	Assuming initial S content for typical 'arc' basalt (Metrich et al., 1999; Delmelle et al., 1999)
600	1.61×10^{12} kg	Assuming initial S content similar to Cerro Negro basalts (Roggensack et al., 1997)
240	4.03×10^{12} kg	S loss based on electron microprobe analysis of Masaya melt inclusions (Stoiber et al., 1986)
96	1.01×10^{13} kg	S loss based on electron microprobe analysis of melt inclusions in recent Masaya bombs (Horrocks, 2001)

2000 value. This compositional shift was accompanied by a factor of 3–5 decrease in SO_2 flux, and an even more dramatic fall in the HCl and HF fluxes, from $\sim$7.6 and 0.9 kg s^{-1} in 1998, to $\sim$0.5 and 0.04 kg s^{-1}, respectively, in 2001. All of these changes occurred prior to the 23 April 2001 phreatic eruption at Masaya. We interpret these as indications of increased magmatic gas scrubbing by a hydrothermal system, selectively removing the more water-soluble species. This increased magmatic–hydrothermal interaction may have been initiated by fracturing of the host rock around the shallow magmatic plumbing system during a sequence of moderate earthquakes that struck the region in July 2000.

Eruptions such as the 2001 Masaya event represent a real challenge to the volcano monitoring and eruption forecasting community, as only rather small overpressures are required to trigger such minor explosions, and precursory geodetic or seismic signals may be subtle or absent altogether. Though small, these events present significant risk due to the increasing numbers of tourists visiting volcanoes, and, of course, to scientists working in the field. Detecting geochemical changes indicative of increased hydrothermal interaction may provide one means for hazard assessment in some of these situations. The versatility and precision of FTS, and potential for deploying remote and automated systems lends itself to operational surveillance.

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