



Investigation into magma degassing at Nyiragongo volcano, Democratic Republic of the Congo

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[1] We report the first combined measurements of the composition and flux of gas emitted from Nyiragongo volcano by ground-based remote-sensing techniques. Ultraviolet spectroscopic measurements made in May/June 2005 and January 2006 indicate average SO₂ emission rates of 38 kg s⁻¹ and 23 kg s⁻¹, respectively. Open-path Fourier transform infrared spectroscopic measurements obtained in May/June 2005, January 2006, and June 2007 indicate average molar proportions of 70, 24, 4.6, 0.87, 0.26, 0.11, and 0.0016% for H₂O, CO₂, SO₂, CO, HCl, HF, and OCS, respectively. The composition of the plume was remarkably similar in 2005, 2006, and 2007, with little temporal variation in proportions of CO₂, SO₂, and CO, in particular, on the scale of seconds or days or even between the three field campaigns that span a period of 24 months. This stability persisted despite a wide range of degassing behaviors on the surface of the summit crater's lava lake (including discrete strombolian bursts and lava fountains) and variations in the SO₂ emission rate. We explain these observations by a regime of steady state degassing in which bubbles nucleate and ascend in chemical equilibrium with the convecting magma. Short-term (seconds to minutes) temporal fluctuations in the SO₂-HCl-HF composition were observed, and these are attributed to shallow degassing processes.

Components: 9346 words, 9 figures, 6 tables.

Keywords: Nyiragongo; volcanic gas emissions; FTIR; DOAS; remote sensing; spectroscopy.

Index Terms: 8430 Volcanology: Volcanic gases; 8485 Volcanology: Remote sensing of volcanoes; 8425 Volcanology: Effusive volcanism.

Received 14 September 2007; **Revised** 15 November 2007; **Accepted** 11 December 2007; **Published** 28 February 2008.

Sawyer, G. M., S. A. Carn, V. I. Tsanev, C. Oppenheimer, and M. Burton (2008), Investigation into magma degassing at Nyiragongo volcano, Democratic Republic of the Congo, *Geochem. Geophys. Geosyst.*, 9, Q02017, doi:10.1029/2007GC001829.

1. Introduction

[2] Nyiragongo volcano (1.52°S, 29.25°E; alt. 3469 m) is located on the western branch of the East African Rift System, approximately 18 km north of the city of Goma (pop. 600,000), in the Democratic Republic of the Congo (DRC) (Figure 1). It forms part of the alkaline Virunga volcanic chain and erupts low viscosity leucite-, melilite-, and nepheline-bearing basanitic lavas [Sahama, 1962, 1973]. Its summit crater is ~1.3 km in diameter and it currently hosts the world's largest (~200 m diameter) persistent lava lake, which is perched ~1.5 km above the altitude of Goma.

[3] In 1977, the first historical effusive eruption occurred when N-S oriented fractures opened on both the northern and southern flanks of Nyiragongo at elevations between 2700 m and 2200 m [Tazieff, 1977]. The lava lake, which had been 155 m below the crater rim before the eruption, drained completely, leaving an empty crater ~1000 m deep. Lava flows, with an estimated total volume of $2.2 \times 10^7 \text{ m}^3$, raced down the flanks of the volcano reaching speeds of up to 60 km h^{-1} , inundating several villages and a significant amount of agricultural land. Between 74 and 400 people were killed [Durieux, 2003]. June 1982 saw the onset of a significant eruption that was confined within the summit crater. Vigorous lava fountaining was observed followed by the reappearance of the lava lake. By September 1982 the level of the lake had risen to 445 m below the summit [Krafft and Krafft, 1983] and by December 1995, following further discontinuous eruptive activity, it was 295 m below the crater rim [Tedesco, 1995]. Observations of volcanic activity between 1995 and 2002 were scarce due to political unrest in DRC.

[4] On 17 January 2002, the second historical flank eruption of Nyiragongo occurred when a series of N-S oriented fractures opened on the upper south flank of the volcano, again triggering drainage of magma stored in the shallow plumbing system. A network of fractures (parallel to preexisting structures of the main rift-related tectonic faults) propagated down slope, and flows of low viscosity pahoehoe and "a" lava issued from numerous dyke-fed vents [Komorowski *et al.*, 2004]. The eruption of $\sim 2.5 \times 10^7 \text{ m}^3$ of magma formed a complex lava flow field which ultimately fed two main flows that destroyed ~13% of Goma and 80% of its economic assets, 1/3 of the airport

runway, and the housing of 120,000 people. There were an estimated 470 injuries and 70–100 deaths. During May 2002 lava fountaining activity was observed on the floor of the summit crater, ~700 m below the crater rim [Global Volcanism Network (GVN), 2002a]. This activity led to the formation of the persistent lava lake, which is active to the time of writing (November 2007).

[5] Since late 2002, satellite remote-sensing data have shown Nyiragongo volcano to be a significant, and persistent, point source of SO_2 to the free troposphere [Carn, 2004]. Ground-based measurements of the plume, however, have been few and far between due to continuing civil and political unrest in the region. Surveillance of SO_2 and other volcanic emissions is important for several reasons. First, acid species in volcanic plumes are known to have deleterious effects on local environments and human health [Baxter *et al.*, 2004] and quantification of emissions provides a basis for further study and mitigation of potential hazards. Second, Nyiragongo's lava lake is a continuing threat to the dense population on the flanks of the volcano, and studies into the magnitude, composition and variability of volatile emissions provide important insights into the transport and supply of magma to the lava lake.

[6] Here we report measurements of gas emissions from the lava lake using two ground-based remote-sensing techniques: (1) zenith sky differential optical absorption spectroscopy (UV-DOAS) to measure column amounts and hence derive fluxes of SO_2 and (2) open-path Fourier transform infrared (FTIR) spectroscopy to derive the proportions of the volcanic gases H_2O , CO_2 , HCl , HF , CO and OCS emitted into the atmosphere. We explore the variability of the plume's composition over time-scales of seconds to hours, and between successive campaigns, and discuss implications of these observations with respect to the volcanic system and degassing processes.

2. Methodology

2.1. UV-DOAS

[7] In May/June 2005 and January 2006 SO_2 emission rates from Nyiragongo were measured using Ocean Optics USB2000 ultraviolet (UV) spectrometers, following the procedures outlined by Galle *et al.* [2002]. The spectrometers were coupled to single lens telescopes and mounted to the roof of a vehicle so that they viewed the zenith sky. The instrumentation was driven underneath the plume at a speed of $\sim 30 \text{ km h}^{-1}$ in a direction



Figure 1. The location of Nyiragongo volcano. The gas plume lay within the shaded region to the SW of the summit crater for all flux measurements performed in 2005 and 2006. Red lines indicate roads, while the yellow and black dotted line represents the border between DRC and Rwanda. (Original image from the National Imagery and Mapping Agency.)

roughly perpendicular to the plume transport direction. The spectrometers were thermo-stabilized at a temperature of $15.0 \pm 0.5^\circ\text{C}$ and spectra were collected every ~ 2 s, between 290 and 432 nm, using Jscripts executed in DOASIS [Kraus, 2006]. The geographical coordinates for each spectrum were determined from the log of a continuously recording GPS unit. All traverses in this study were made along the road from Goma to Sake (Figure 1), which is at an altitude of 1500 m asl and approximately 17 km from the active crater. In some instances, when the plume was carried toward the WSW, traverses could not be completed due to poor roads beyond Sake. These data have been omitted.

[8] SO_2 columns were retrieved from each measured spectrum following standard differential optical absorption spectroscopy procedures outlined by Platt [1994] and Oppenheimer et al. [2004]. The optimal fitting window, 309.62–340.00 nm, was found by searching for a near random fit residual structure with minimal standard deviation. The reference spectra included in the non-linear fit were obtained by convolving high-resolution SO_2

[Rufus et al., 2003] and O_3 [Burrows et al., 1999] cross-sections with the instrument line shape (FWHM = 0.45 nm). A Fraunhofer reference spectrum and a Ring spectrum, calculated using DOASIS, were also included in the fit.

[9] Retrieved column amounts of SO_2 were projected on to the plane perpendicular to the plume trajectory and SO_2 emission rates were obtained from the product of the integrated SO_2 column amounts across this plane, and the plume speed. Here plume speeds have been derived from the ARPEGE climate model [Deque et al., 1994] used by the Toulouse Volcanic Ash Advisory Center, which monitors eruption clouds from African volcanoes. On the basis of visual observations of the plume's altitude we used wind speed data modeled at 500 hPa (~ 5.6 km altitude) to approximate the plume speed on 18 May, 20 May and 1 June 2005 and wind speed data modeled at 700 hPa (~ 3 km altitude) to approximate the plume speed on 6, 7 and 14 January 2006.

[10] It should be noted that errors in flux measurements tend to be high, primarily due to errors in

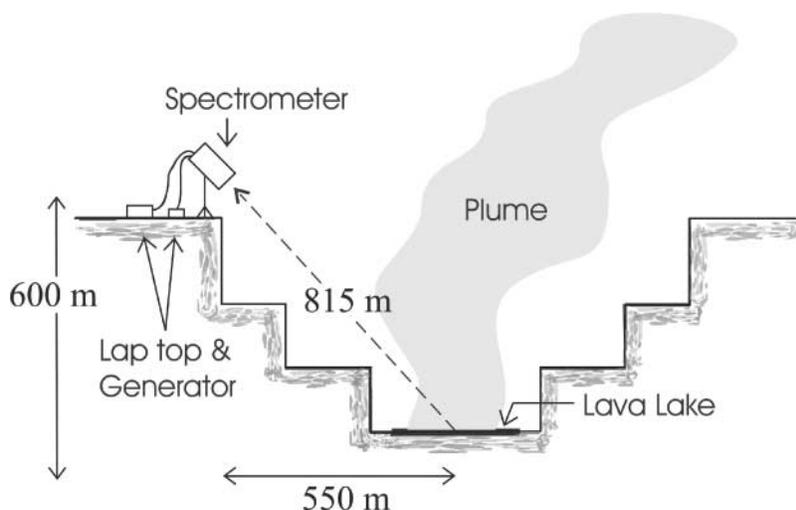


Figure 2. Cartoon illustrating the FTIR spectrometer configuration at the summit of Nyiragongo volcano.

plume speed estimates [Stoiber *et al.*, 1983]. This is true of measurements at Nyiragongo, particularly given the complexity of wind fields around the steep-sided volcano. Additional errors are also introduced through multiple scattering [Weibring *et al.*, 2002], variable cloudiness along the traverse, SO₂ depletion [Oppenheimer *et al.*, 1998] and the presence of volcanic ash in the plume [Andres and Schmid, 2001]. Geometrical concerns such as the error in the distance perpendicular to the plume transport direction determined between adjacent GPS points, and the error in the angle between the assumed wind direction and the traverse path should also be considered [Mather *et al.*, 2006].

2.2. FTIR Spectroscopy

[11] Plume composition measurements were made in May/June 2005, January 2006 and June 2007 using a portable MIDAC FTIR spectrometer equipped with interchangeable MCT or InSb detectors with sensitivities between 600 and 5000 cm⁻¹ and 1800 and 6000 cm⁻¹, respectively. Absorption spectra were collected at 0.5 cm⁻¹ resolution over periods of between one and five hours, on three days in 2005 (25, 26 and 27 May), two days in 2006 (9 and 11 January) and three days in 2007 (18, 19 and 20 June). We used the lava lake as a source of infrared (IR) radiation, as illustrated in Figure 2. The spectrometer was set up on the southeastern crater rim and aligned to view a persistently active region on the western side of the lake (Figure 3). Measurements with laser range-finding binoculars, made by M. Kasereka of the Goma Volcano Observatory (GVO), showed the distance from the lava lake to the spectrometer to

be approximately 820 m in 2005 and 810 m in January 2006. Visual observations suggested a comparable optical path length for measurements in June 2007. The nominal field of view of the spectrometer was 20 mrad (we did not use a telescope) and atmospheric temperatures and pressures at the crater rim were between 280 and 285 K and 680 and 690 hPa, respectively. Four consecutive spectra were co-added in order to improve the signal-to-noise ratio in the recorded spectra resulting in a time step of ~4 s.

[12] To retrieve column amounts of IR-active gases (H₂O, CO₂, SO₂, HCl, HF, CO, OCS, CH₄ and N₂O) present in the path between the source of IR radiation and the detector, IR spectra were first simulated in specified frequency microwindows (Table 1) via a radiative transfer forward model (the RFM [Edwards and Dudhia, 1996]) using line parameter data from the HITRAN database [Rothman *et al.*, 2005] together with estimates for pressure, temperature and initial column amounts, specified for both atmospheric and volcanic gas species. The simulated spectra were fitted to the measured spectra using an optimal estimation algorithm [Rodgers, 1976] and a non-linear least squares fitting procedure [Marquardt, 1963]. The retrieval yields an estimate of the error, which is based on the standard deviation of the residual across the spectral window used for the fit. For further details on the retrieval procedure, see Burton [1999].

[13] It should be noted that derivation of gas column amounts from FTIR spectra requires no direct knowledge of the temperature of the source,

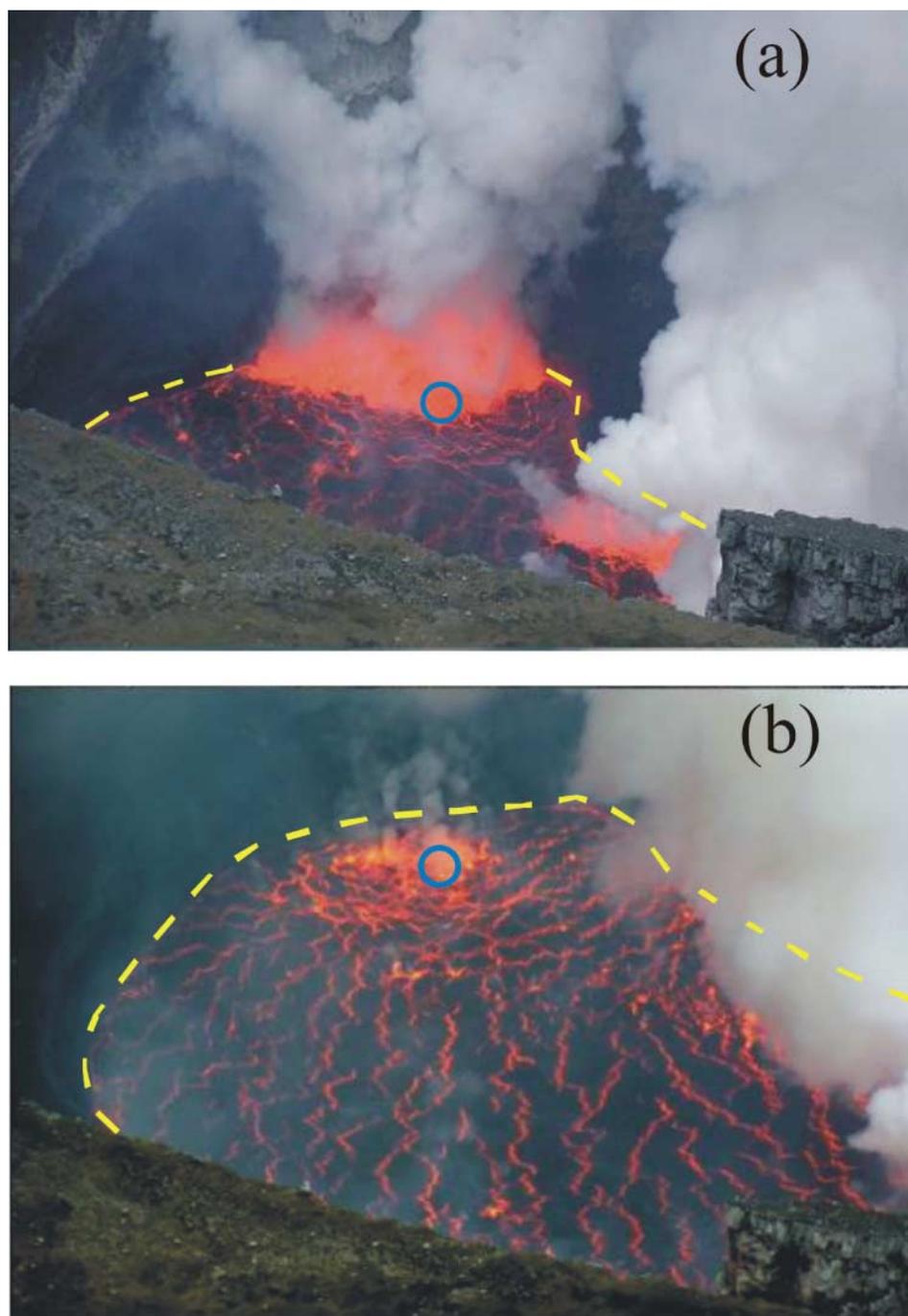


Figure 3. Nyiragongo's lava lake photographed from the FTIR spectrometer observation site on the southeastern rim of the summit crater. The yellow dashed line represents the edge of the lake, and blue circles approximate the ~16 m footprint of the FTIR spectrometer: (a) 27 May 2005, (b) 9 January 2006, and (c) 19 June 2007. Note the same rock outcrop at the bottom of each photograph.

as the original intensity is implicitly fitted during analysis. Emission of radiation by hot gases, however, should be considered as it becomes important when the difference between source and gas tem-

perature is small, particularly at longer wavelengths. Here, measurements made with a FLIR (Forward Looking InfraRed) P25 thermal camera, from the same location as the FTIR spectrometer,

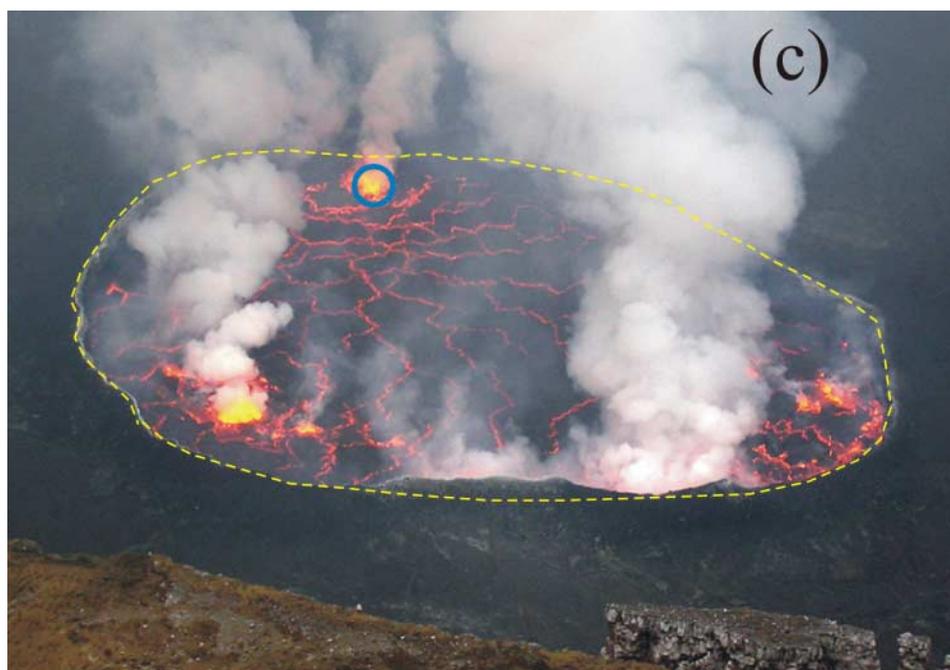


Figure 3. (continued)

showed a temporally averaged temperature of 1250 K over the FOV of the spectrometer. (Images were corrected for attenuation by atmospheric and volcanic gases following *Sawyer and Burton* [2006]). When gas is expelled from the lava lake it cools rapidly due to mixing with large volumes of air and as a result, for any given measurement, a small proportion of gas, close to the magma, will be at high temperature while the majority of gas will be significantly cooler. Due to the high temperature dependency of the rotational line structure in the 2500 cm^{-1} spectral band of SO_2 we were able to retrieve the predominant volcanic gas temperature along the measurement path for each spectrum, by including it as a parameter during SO_2 analysis. All retrieved volcanic gas temperatures lay in the range 300 K to 540 K, with the best spectral fit for the majority of spectra produced with a gas temperature of ~ 360 K. Assuming a source temperature of 1250 K and a gas temperature of 540 K we estimate, on the basis of radiative transfer calculations using the RFM and HITRAN database, that just $\sim 0.20\%$ of the absorbed radiation is re-emitted over the wavelength range 4070 to 4210 cm^{-1} , and $\sim 4.0\%$ of the absorbed radiation is re-emitted over the range 2020 to 2100 cm^{-1} . As a result we consider the emission of radiation by the plume to be negligible. An example of a spectral fit for SO_2 , illustrated in Figure 4, shows that despite the range of plume temperatures along the optical path, using

a single gas temperature in the retrieval yields high quality fits.

3. Results

3.1. SO_2 Flux Measurements

[14] SO_2 flux data collected in May/June 2005 and January 2006 are given in Table 2. The average SO_2 emission rate calculated from 7 traverses in 2005 was $\sim 38\text{ kg s}^{-1}$ (3330 t d^{-1}). In January 2006, the average emission rate from a total of 8 traverses was $\sim 23\text{ kg s}^{-1}$ (2180 t d^{-1}).

3.2. Plume Composition Measurements

[15] Analysis of FTIR spectra yielded time series of H_2O , CO_2 , SO_2 , HCl , HF , CO , OCS , CH_4 and

Table 1. Spectral Microwindows Used for Fitting the Listed Gas Species

Gas	Spectral Window, cm^{-1}
H_2O	2700–2800
CO_2	2020–2100
SO_2	2440–2540
CO	2095–2205
HCl	2690–2830
HF	4070–4210
OCS	2000–2100
CH_4	2740–2920
N_2O	2155–2240

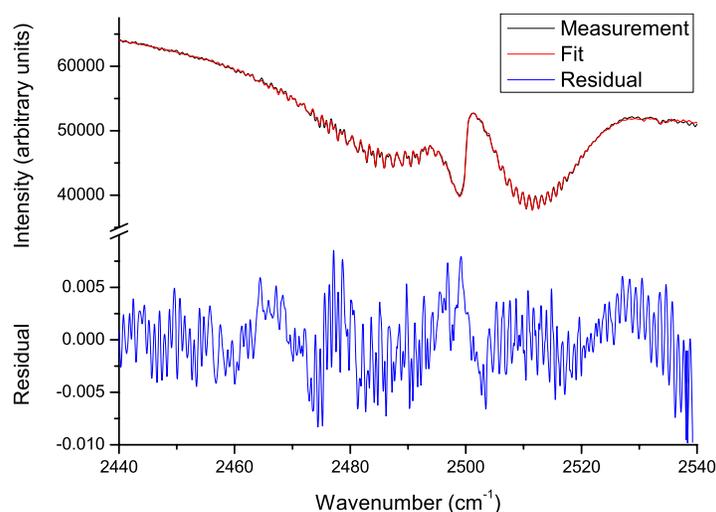


Figure 4. Example of a fitted SO₂ spectrum. The top trace shows a typical measured spectrum of SO₂ (black) acquired on 9 January 2006 with the fitted spectrum (red) overlaid. The bottom trace shows the residual of the fit (blue), which is equal to [(measured spectrum - fitted spectrum)/measured spectrum]. The near-random structure and low amplitude seen in the residual illustrate the high quality of the fit.

N₂O column amounts. An example series, from 27 May 2005, is shown in Figure 5. It is clear that column amounts of volcanic gas species fluctuate considerably from one spectrum to the next, due to variations in atmospheric transport and observed discontinuous emission from the lava lake. The traces for N₂O and CH₄, however, are approximately flat, indicating that these species are present in the ambient atmosphere but not detectable in emissions from the lava lake.

[16] As a validation of the accuracy of our gas retrievals, average retrieved column amounts of CH₄ and N₂O from all measured spectra were calculated and converted to atmospheric mixing ratios. Values of 2.45×10^{18} molecules cm⁻² and 4.5×10^{17} molecules cm⁻², over the 815 m path length, correspond to ~ 1.71 ppmv and ~ 0.31 ppmv for CH₄ and N₂O, respectively. These values are in good agreement with typical tropospheric mixing ratios [Seinfeld and Pandis, 2006].

[17] While the path amounts of individual volcanic gases themselves are not informative, plotting column amounts of two volcanic gas species against each other and fitting a regression line to the data allows the ratio of the two species to be obtained. Figure 6 shows each retrieved volcanic gas (*X*) plotted against SO₂ where, in each case, the gradient of the regression line represents *X*/SO₂ molar ratios. In the cases of H₂O and CO₂, the offsets on the *y* axis represent the ambient atmospheric component of these species. The CO₂ intercept of $\sim 6 \times 10^{20}$ molecules cm⁻² corre-

sponds to an atmospheric mixing ratio of 420 ppmv. This value is higher than the expected ambient background concentration of CO₂ (~ 370 ppmv), and may be due to diffuse CO₂ emissions from around the crater rim or to regional environmental effects. We have only presented data collected over a three-hour time period on 27 May 2005, a one-hour 45 minute period on 9 January 2006 and a one-hour 40 minute period on 19 June 2007 because the relative humidity remained stable during these times, allowing volcanic water vapor to

Table 2. SO₂ Fluxes Measured at Nyiragongo in May/June 2005 and January 2006^a

Date	Time, UT	Wind Speed, m s ⁻¹	SO ₂ Flux, kg s ⁻¹
18 May 2005	1350	7.72	56
18 May 2005	1445	7.72	35
20 May 2005	1229	5.14	38
20 May 2005	1255	5.14	29
20 May 2005	1325	5.14	47
20 May 2005	1353	5.14	29
1 Jun 2005	1303	5.14	33
6 Jan 2006	0900	5.14	30
6 Jan 2006	0944	5.14	14
6 Jan 2006	1016	5.14	36
7 Jan 2006	0915	6.43	14
7 Jan 2006	0950	6.43	19
7 Jan 2006	1020	6.43	11
7 Jan 2006	1059	6.43	24
14 Jan 2006	1437	5.14	32

^aWind speed data have been derived from the ARPEGE climate model.

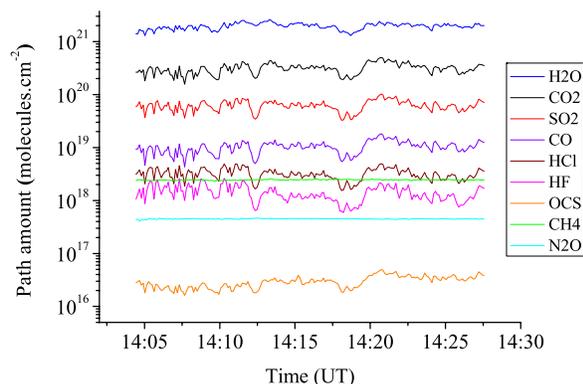


Figure 5. Example time series of retrieved gas path amounts from FTIR spectra collected on 27 May 2005 (1403 to 1428 UT). Atmospheric background amounts of H₂O and CO₂ have been subtracted, leaving only volcanic contributions.

be accurately constrained. By multiplying X/SO_2 mass ratios by SO₂ fluxes obtained using UV-DOAS, we estimate fluxes of other gases emitted from Nyiragongo (Table 3).

4. Discussion

4.1. Gas Flux

[18] Prior to the 2002 eruption of Nyiragongo, only sporadic observations of gas emissions from the central crater were recorded [e.g., *GVN*, 1994a, 1994b, 1996, 2001; *Krafft and Krafft*, 1983; *Scientific Event Alert Network*, 1977a, 1977b; *Tazieff*, 1977, 1979, 1984, 1994]. Semi-quantitative estimates of gas flux were made by *Delsemme* [1960] and by *Le Guern* [1987] using video footage to estimate the plume's dimensions and rise rate. In conjunction with compositional data obtained by direct sampling [*Chaigneau et al.*, 1960; *Le Guern*, 1987], the fluxes of H₂O, CO₂ and SO₂ were estimated to be 56, 133 and 17 kg s⁻¹ during the 1959 expedition and 890, 2130 and 260 kg s⁻¹ during 1972. The high level of degassing in the early 1970s is consistent with the voluminous plume observed at that time [*Tazieff*, 1979].

[19] Between 1978 and 2005, the Total Ozone Mapping Spectrometer (TOMS) instruments observed eruptive SO₂ emissions from Nyamuragira [*Bluth and Carn*, 2008; *Carn and Bluth*, 2003], a volcano approximately 20 km NW of Nyiragongo. No emissions from Nyiragongo were observed by TOMS, however, until the eruption on 17 January 2002 when an SO₂ plume extending westward from the summit region was detected at 09.08

GMT. The cloud contained 9.3 ± 2.8 kt of SO₂ which equates to an average emission rate of $\sim 850\text{--}1700$ kg s⁻¹ for the first two to three hours of the eruption [*Carn*, 2004]. No TOMS data were collected over the Virunga region on 18 January 2002 and no further emissions were detected during subsequent months. In September 2002, however, reports of a strong plume were made [*GVN*, 2002b] and from 7 October 2002 to 17 November 2003 regular SO₂ emissions from Nyiragongo were detected by TOMS, with average fluxes estimated to be 185 kg s⁻¹ [*Carn*, 2004].

[20] If we assume the average gas ratios measured in this study by FTIR spectroscopy are representative of those in 2002/2003 we obtain fluxes of H₂O, CO₂, CO, HCl, HF and OCS over that period of 793, 655, 15, 5.8, 1.4 and 0.09 kg s⁻¹, respectively. Of particular note is the high CO₂ emission rate: 655 kg s⁻¹ equates to ~ 21 Tg a⁻¹ which is significantly higher than the estimated CO₂ flux of 13 ± 3 Tg a⁻¹ emitted from the summit craters at Mt. Etna, Italy [*Allard et al.*, 1991], an alkaline volcano regarded as the strongest contemporary volcanic source of CO₂.

[21] Ground-based measurements performed by *Galle et al.* [2005] in March and April 2004 yielded average SO₂ emission rates of 79 kg s⁻¹ and 102 kg s⁻¹, respectively; all flux measurements made at Nyiragongo prior to this study are summarized in Table 4. Since September 2004, SO₂ burdens in the Nyiragongo volcanic plume have been monitored by the space-based Ozone Monitoring Instrument (OMI) [*Krotkov et al.*, 2006] (Figure 7). Our observation of a lower SO₂ flux in January 2006 (23 kg s⁻¹) compared to May/June 2005 (38 kg s⁻¹) is consistent with the OMI measurements and represents a significant decline in SO₂ flux compared to the period of intense degassing noted in 2002/2003.

[22] Inferred fluxes of H₂O, CO₂, CO, HCl, HF and OCS during our observation periods are given in Table 3. While emission rates of all species are lower than they were estimated to be in 2002/2003, they are still significant compared to many other passively degassing volcanoes. For example, CO₂ fluxes are higher than those measured at Masaya (32–36 kg/s [*Burton et al.*, 2000]), an open-vent volcano on the Central American Arc in Nicaragua, and at Mt. Erebus, Antarctica (22 kg/s [*Wardell et al.*, 2004]), an alkaline volcano renowned for its CO₂-rich plume. Few data on volcanic emission rates of CO are available in the literature, but our values are comparable to Mt. Erebus (1.74 kg/s

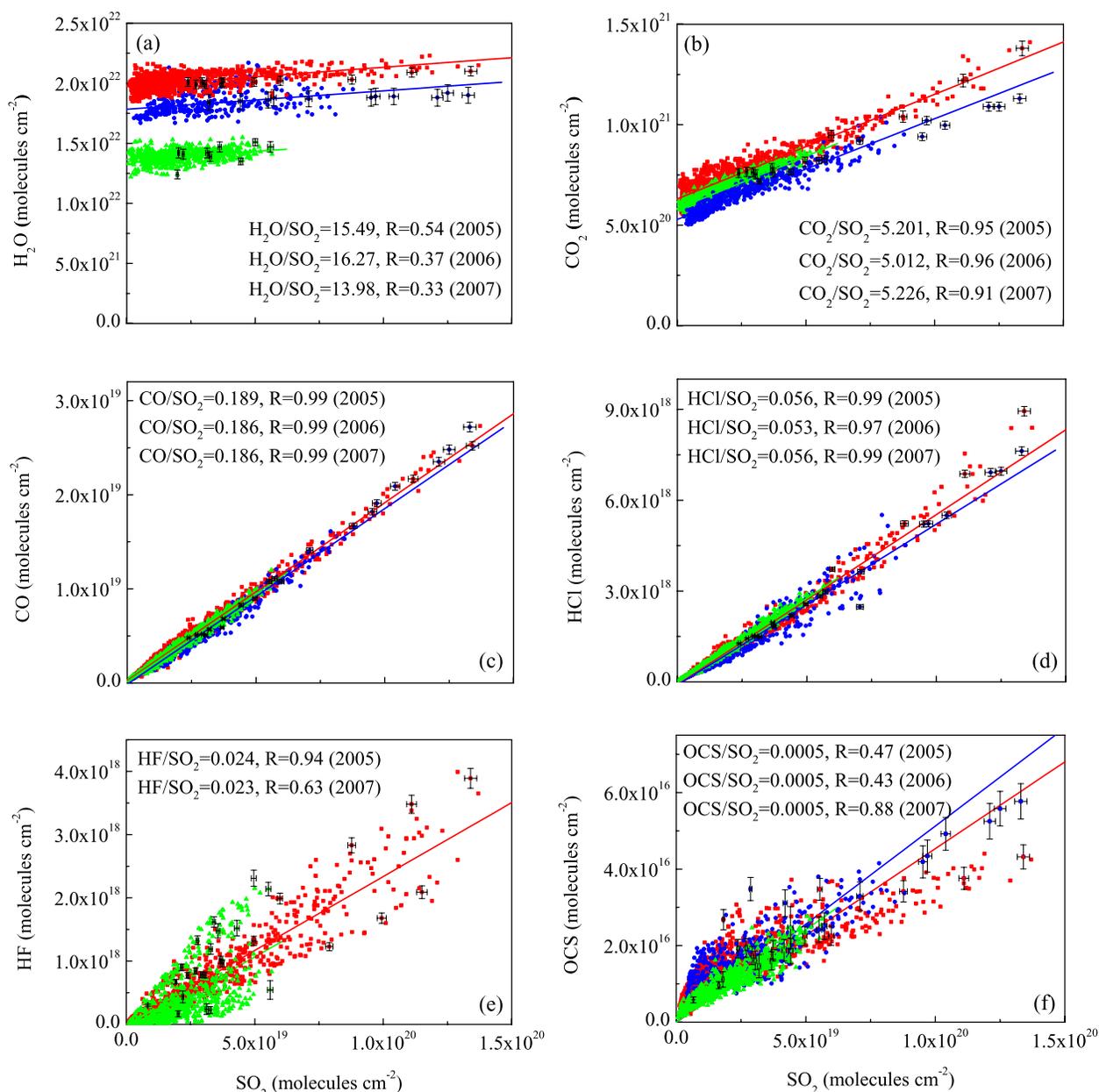


Figure 6. Scatterplots showing column amounts of each volcanic gas species versus SO₂. (a) H₂O, (b) CO₂, (c) CO, (d) HCl, (e) HF, (f) OCS. Red squares represent data from 27 May 2005, blue diamonds are from 9 January 2006, and green triangles are from 19 June 2007. Typical error bars derived from the output of the retrieval algorithm are shown.

[Wardell *et al.*, 2004]) and higher than those observed at Oldoinyo Lengai (0.08 kg/s [Oppenheimer *et al.*, 2002]), a carbonatite volcano on the East African Rift zone. Halogen emissions (HCl and HF) from Nyiragongo are lower than typical emissions from Mt. Etna (8.2 and 2.2 kg/s, respectively [Francis *et al.*, 1998]) and Masaya (7.4 and 0.91 kg/s, respectively [Burton *et al.*, 2000]) but comparable with emissions from Villarrica (1.3 and 0.3 kg/s, respectively [Mather *et al.*, 2004]), a predominantly basaltic, open-vent volcano situated

in the southern Chilean Andes. Emissions of OCS are comparable with estimates for active basaltic volcanoes presented by Belviso *et al.* [1986] (0.002 to 0.016 kg s⁻¹).

4.2. Plume Composition

[23] From Figure 6 and Table 3 we see that the average measured plume composition was remarkably similar in 2005, 2006 and 2007, which suggests steady state degassing at Nyiragongo volcano over the considered 24 month period. This stability

Table 3. X/SO_2 Molar and Mass Ratios in the Plume Emitted From Nyiragongo Volcano in May/June 2005, January 2006, and June 2007 and the Inferred Flux of Each Species in 2005 and 2006^a

Gas	May/June 2005			January 2006			June 2007	
	Molar Ratio (X/SO_2)	Mass Ratio (X/SO_2)	Inferred Flux, kg s^{-1}	Molar Ratio (X/SO_2)	Mass ratio (X/SO_2)	Inferred Flux, kg s^{-1}	Molar Ratio (X/SO_2)	Mass Ratio (X/SO_2)
H ₂ O	15.49	4.36	167.8	16.27	4.58	103.4	13.98	3.93
CO ₂	5.20	3.58	137.7	5.01	3.45	77.9	5.23	3.60
SO ₂	1.00	1.00	38.4	1.00	1.00	22.6	1.00	1.00
CO	0.189	0.083	3.18	0.186	0.082	1.84	0.186	0.081
HCl	0.056	0.032	1.23	0.053	0.030	0.69	0.056	0.032
HF	0.024	0.007	0.29	n.m.	n.m.	n.m.	0.023	0.007
OCS	0.0005	0.0005	0.018	0.0005	0.0005	0.011	0.0005	0.0005

^aNote: “n.m.” indicates the gas was not measured due to insufficient signal reaching the detector of the FTIR spectrometer at frequencies above 4000 cm^{-1} .

is reminiscent of the stability recognized at Masaya volcano over a comparable timescale [Horrocks *et al.*, 1999].

4.2.1. Comparison of Gas Composition With Previous Studies

[24] If we assume that all the major gas phase constituents of the plume were measured by FTIR spectroscopy, we can normalize the X/SO_2 ratios presented in Table 3 and deduce molar proportions of each species (Table 5). Comparison of our data with data obtained from plume samples collected at Nyiragongo in 1959 and 1972 (reported by *Le Guern* [1987]) (renormalized to exclude H₂S, H₂ and S₂, which together typically make up a few mole percent) illustrates some significant differences (Table 5). In particular, we observed higher proportions of H₂O and SO₂ and lower proportions

of CO₂ than were measured in 1959 and 1972. We suggest these differences could either be a result of long-term progressive depletion of CO₂ from the source region that supplies the long-lived Nyiragongo lava lake, or, considering the consistency of the gas composition in 1959 and 1972 and the consistency of our data from 2005 to 2007, it is possible that an entirely different batch of magma is now feeding the Nyiragongo lava lake. To gain a better insight into the long term degassing trend at Nyiragongo, further long-term sampling and FTIR spectroscopic measurements are required.

4.2.2. Comparison of Gas Composition With Other Volcanoes

[25] In order to contextualize gas emissions from Nyiragongo (a divergent-plate, alkaline volcano), we compare data obtained here with those obtained

Table 4. SO₂ Flux Measurements Performed at Nyiragongo Prior to This Study

Date	Time, UT	Wind Speed, m s^{-1}	SO ₂ Flux, kg s^{-1}	Method ^a
1959	-	N/A	17 ^b	video footage and plume composition
1972	-	N/A	260 ^c	video footage and plume composition
17 Jan 2002	0908	N/A	850–1700 ^d	TOMS data representing the first 2–3 hours of eruptive activity
7 Oct 2002 to 17 Nov 2003	-	N/A	an average of 185 ^d	TOMS data
9 Mar 2004	0859	5	65 ^e	UV-DOAS (V.T.)
9 Mar 2004	0927	5	88 ^e	UV-DOAS (V.T.)
9 Mar 2004	1002	5	70 ^e	UV-DOAS (V.T.)
15 Mar 2004	0833	not specified	47 ^e	UV-DOAS (H.T.)
15 Mar 2004	0841	not specified	60 ^e	UV-DOAS (H.T.)
15 Mar 2004	0851	not specified	78 ^e	UV-DOAS (H.T.)
5 Apr 2004	0841	5	114 ^e	UV-DOAS (V.T.)
5 Apr 2004	0921	5	90 ^e	UV-DOAS (V.T.)

^aV.T., vehicle traverse; H.T., helicopter traverse.

^b*Delsemme* [1960], reported by *Le Guern* [1987].

^c*Le Guern* [1987].

^d*Carn* [2004].

^e*Galle et al.* [2005].

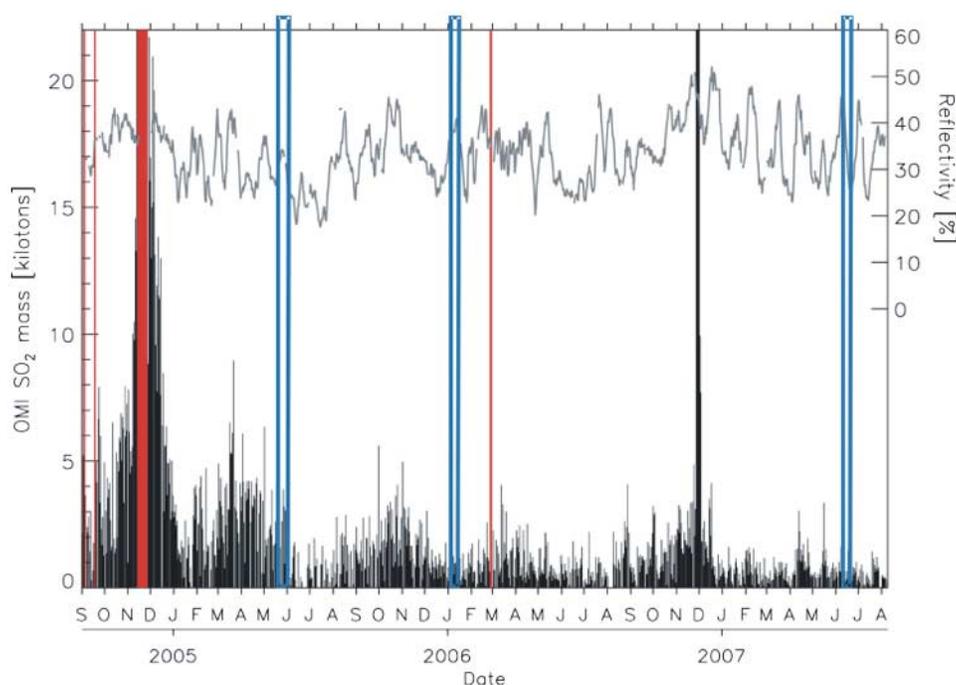


Figure 7. Instantaneous SO_2 burdens in the Nyiragongo volcanic plume measured by the Ozone Monitoring Instrument since September 2004. Note there are several data gaps in late 2004; data gaps of >1 day are indicated by red bars. Blue rectangles represent our ground-based measurement periods, and the grey curve shows UV reflectivity, a proxy for cloud cover on each day. (The large signal in November–December 2006 is due to an eruption of nearby Nyamuragira volcano).

from volcanoes from a variety of tectonic settings as presented by *Symonds et al.* [1994], *Allard and Burton* [2004] and *Burton et al.* [2000] (Table 6). First, we see that our observed $\text{H}_2\text{O}/\text{CO}_2$ ratios (~ 3.0) are low compared to convergent-plate volcanoes such as Augustine, Masaya, Merapi, Momotombo, Mount St. Helens, Poas, Showa-Shinzan and Usu (whose $\text{H}_2\text{O}/\text{CO}_2$ ratios range from 20.5 to 1633). They are also low compared to other divergent plate volcanoes such as Ardoukoba, Erta “Ale and Surtsey (whose ratios range from 4.9 to 29.8) and to the convergent-plate, alkaline volcano, Mt. Etna ($\text{H}_2\text{O}/\text{CO}_2 \sim 6.5$). Our $\text{H}_2\text{O}/\text{CO}_2$ ratios are higher than those measured at Kīlauea’s summit but significantly lower than those measured on the East Rift Zone (ERZ), approximately 15 km away from the summit caldera. The difference in ratios at Kīlauea is due to extensive depletion of CO_2 via summit degassing, prior to magma reaching the ERZ. These observations on $\text{H}_2\text{O}/\text{CO}_2$ ratios reflect the low concentrations of H_2O in divergent-plate magmas compared with convergent-plate magmas, which contain significant volumes of subducted seawater [*Giggenbach*, 1992], and the high proportions of CO_2 in gases from alkaline magmas [*Gerlach*, 1982]. Accordingly, our observed CO_2/SO_2 ratios

(~ 5.1) are high when compared to data from other, aforementioned, divergent-plate volcanoes (typically in the range 0.27 to 1.9), Kīlauea (2.2 at the summit and 0.26 at the ERZ) and Etna (3.5) but fall within the range observed at convergent-plate volcanoes (0.49 to 21.2). SO_2/HCl ratios (~ 18.2) are similar to those of high temperature gases from Erta “Ale (~ 17.6), but significantly different from gases from other tectonic settings. The considered convergent-plate volcanoes have SO_2/HCl ratios between 0.15 and 3.3 (and 9.7 at Etna), due to enrichment of Cl in the parent magmas [*Giggenbach*, 1992], while gas emissions from Kīlauea are HCl-poor and hence ratios are >78.0 at the summit and ~ 9 on the ERZ. Finally, our HCl/HF ratios (~ 2.4) are lower than those observed at the convergent-plate volcanoes (which have HCl/HF ratios in the range 2.5 to >39.2) but higher than those observed on Kīlauea’s East rift zone (0.91).

4.2.3. Degassing Mechanisms

[26] While rigorous interpretation of our observed gas ratios is precluded by a current lack of data on the original (or final) volatile contents of Nyiragongo magma, or on the solubility of volatiles in the melt, the high temporal resolution of our data coupled with visual observations of the lava lake

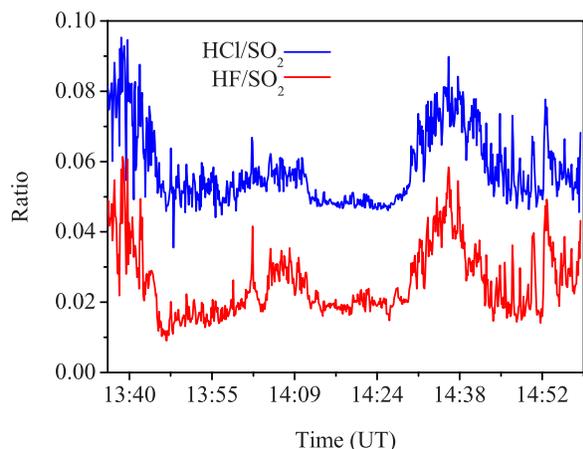


Figure 8. Example of a time series of HCl/SO₂ and HF/SO₂ ratios. Data were collected from 1336 to 1459 UT on 27 May 2005.

surface allows some important constraints on the degassing regime to be deduced. These are discussed in the following paragraphs.

[27] In a recent article, Parfitt [2004] summarized two physical models of gas release from basaltic systems. The first, known as the collapsing foam (CF) model [Jaupart and Vergnolle, 1988, 1989], assumes that gas bubbles accumulate within a storage region at depth and become close packed to form a foam layer. When a critical thickness is reached the foam layer becomes unstable and collapses to form a gas pocket, which ascends rapidly through a magma column to the surface. In this model, fountaining activity occurs from complete almost instantaneous foam collapse whereas strombolian eruptions represent repeated partial foam collapse events. The alternative degassing model is dependent on the rise speed of the magma within the conduit and is known as the rise speed dependent (RSD) model [Parfitt and Wilson, 1995]. If the rise speed of the magma is relatively high then it is assumed that bubbles do not travel far through the overlying magma before the magma itself is erupted. This situation is termed closed-system degassing, and in this way, a continuous stream of bubbles is transported to the surface via magma convection and lava fountaining activity is observed as gas escapes to the atmosphere. If the magma rise speed is low, however, gas bubbles are thought to separate from the melt and rise through the magma column. This is known as open-system degassing. A wide range of bubble sizes may be present in the magma, and the larger bubbles rise faster and are able to coalesce with the smaller bubbles that they intercept. A

runaway situation can be achieved producing a slug of gas that results in a strombolian explosion at the surface. Parfitt [2004] concludes that neither of these models is fundamentally flawed and that either might operate under different starting conditions.

[28] Volatiles such as CO₂, H₂O, SO₂, HCl and HF tend to exsolve from magma at different pressures (depths) and hence temporal variations in the proportions of these species in gas emissions at the surface, coupled with observations of styles of eruptive activity, can provide valuable clues to discriminate between the two models. Allard *et al.* [2005], for example, used high time resolution FTIR spectroscopy to measure gas emissions during an eruption at Mt. Etna, and showed that gas emitted during lava fountaining had significantly higher CO₂/SO₂ and SO₂/HCl ratios compared to quiescent Etnean emissions. The authors concluded that the activity had been driven by a separate ascent of a gas layer that had accumulated ~1.5 km below the erupting crater. Shinohara and Witter [2005], on the other hand, observed stable CO₂/SO₂ and H₂O/CO₂ ratios at Villarrica volcano, even though they observed mild strombolian activity, intermittent lava spattering and continuous quiescent degassing during their measurement period. It was suggested that, in this case, the mild strombolian activity and lava spattering was not driven by bubbles that had accumulated at depth but instead caused by bursting of bubbles formed under equilibrium with the magma.

[29] Video and thermal camera footage taken during field campaigns on Nyiragongo captured a highly dynamic, fast moving (often >1 m s⁻¹) lava lake surface. Rapid variations in the location, magnitude and surface extent of degassing zones were noted and observable degassing behaviors included high-pressure jets, lava fountains, small strombolian explosions and quiescent exhalation from calm surfaces. These degassing manifestations occurred simultaneously from three dominant gas emission points, one on the western side, one on the northeastern side, and one below the observation site on the southeastern side of the lake (Figure 3). In 2005 the western gas emission point was acting as a sink for crusted sections of the lake, whereas in 2006 and 2007, it was a site of magma upwelling. While the FTIR spectrometer was always aligned with the western gas emission point, varying wind directions within the crater carried the plume from different emission sites into the optical path. In this way our measurements repre-

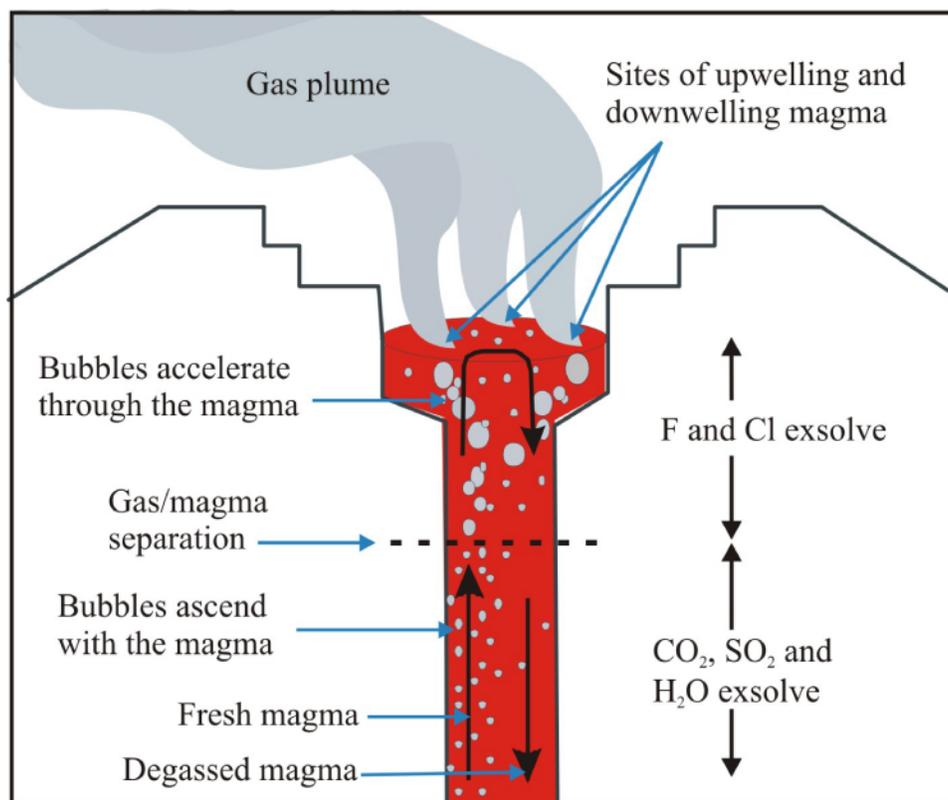


Figure 9. The inferred mechanism of degassing at Nyiragongo. As fresh magma rises up the conduit, the pressure decreases and gas bubbles begin to nucleate. These bubbles initially rise at a speed similar to the ascending magma and hence are able to continually equilibrate. As the gas bubbles (composed primarily of CO_2 , H_2O , and SO_2) grow and become more buoyant, they eventually segregate from the melt and rise through the overlying degassing magma, thereby becoming enriched in more soluble gases (particularly HF and HCl). Gas emissions measured at the surface therefore are a superposition of gas that has evolved in equilibrium with the magma and gases released at shallow depths above the gas/magma separation region. Once gas has been lost to the atmosphere, a relatively dense degassed magma is left behind, which sinks back down the conduit, allowing fresh magma to ascend.

sent the composition of gas that has been released from different regions of the lake, by the various degassing styles.

[30] Although the average composition of the plume was stable from May 2005 to June 2007, close inspection of FTIR spectroscopic data highlights small compositional variations over time-scales of seconds to minutes, as evidenced by the scatter in Figure 6. Fluctuations in the SO_2 –HCl–HF composition (Figures 6d and 6e) are particularly interesting. We believe these fluctuations are real and not due to measurement or retrieval errors since all spectra are of high quality and the retrieval errors are low (Figure 6). Further evidence is provided by comparison of temporal variations in HCl/ SO_2 and HF/ SO_2 ratios. As illustrated in Figure 8 variations in HCl/ SO_2 ratios mirror those in HF/ SO_2 , an observation that is not repeated for other X/SO_2 ratios. The observed temporal varia-

tions in OCS/ SO_2 ratios (Figure 6f) are due primarily to errors in the retrieval, resulting from the low column amounts in the plume although real short-term fluctuations cannot be ruled out. Volcanically significant deviations in $\text{H}_2\text{O}/\text{SO}_2$ ratios (Figure 6a) may also be present, but if so are obscured by the natural variability of atmospheric water content along the optical path. In contrast with HCl/ SO_2 , HF/ SO_2 , $\text{H}_2\text{O}/\text{SO}_2$ and OCS/ SO_2 , the variability of CO_2/SO_2 and CO/SO_2 ratios over the reported measurement periods was low (Figures 6b and 6c) despite the wide range of degassing behaviors and varying gas emission rates that were observed.

[31] To explain our observations we assume a solubility hierarchy for Nyiragongo that is typical of basaltic systems, $\text{CO}_2 < \text{H}_2\text{O} < \text{SO}_2 < \text{HCl}$, HF [e.g., Allard *et al.*, 2005; Burton *et al.*, 2003], and suggest a degassing mechanism (Figure 9) that is

Table 5. Analyses of Gas Composition at Nyiragongo^a

Gas	Mol%				
	1959	1972	May/June 2005	January 2006	June 2007
H ₂ O	47.61	48.99	70.54	72.25	68.28
CO ₂	47.59	45.33	23.68	22.25	25.54
SO ₂	2.39	2.74	4.55	4.44	4.88
CO	2.38	2.94	0.86	0.83	0.91
HCl	n.c.	n.c.	0.26	0.24	0.27
HF	n.c.	n.c.	0.11	n.m.	0.11
OCS	0.083	n.c.	0.0023	0.0022	0.0024

^a Abbreviations: n.c., not calculated; n.m., not measured.

consistent with the RSD model. As fresh magma rises up the conduit from depth, the pressure decreases and CO₂ gas bubbles begin to nucleate. These bubbles increase in volume by decompression and further exsolution of volatiles (primarily CO₂, H₂O, SO₂). They rise at a similar speed to the ascending magma and hence continually equilibrate, resulting in the stable ratio between CO₂ and SO₂ that is observed at the surface. If degassing followed the CF model, or if bubbles were rising out of equilibrium with the magma, then we would expect to see temporal variation in the CO₂/SO₂ ratio as bubbles of different sizes, or sourced at different depths, reached the surface [Allard *et al.*, 2005; Burton *et al.*, 2007; Oppenheimer *et al.*, 2006; Shinohara and Witter, 2005]. As bubbles grow they become more buoyant and, eventually, segregate from their parent magmas and rise through the overlying degassing magma. This transition from closed- to open-system degassing is described by Burton *et al.* [2007] for quiescent degassing from Stromboli volcano, Italy. At some depth close to or above the transition, bubbles become enriched in more soluble gases (particu-

larly HF and HCl), which begin to exsolve from the melt at shallower levels within the conduit. The amount of enrichment is dependent on the size and ascent rate of the bubbles as well as the solubility and speciation of the gases as a function of pressure and redox conditions and the kinetics of volatile diffusion in the melt [Carroll and Webster, 1994]. We suggest the fluctuations in the SO₂–HCl–HF composition we observe are a result of these processes. Streams of bubbles take paths of least resistance to the surface, which coincide with locations of upwelling and downwelling magma, and the type of eruptive activity observed at the surface is determined by the extent to which bubbles coalesce after segregation from their parent magmas. Fountaining results from a continuous stream of discrete bubbles, whereas strombolian bursts occur when a greater degree of coalescence has occurred and larger bubbles reach the surface. Once gas has been lost to the atmosphere a relatively dense degassed magma is left behind, which sinks back down the conduit, allowing fresh magma to ascend.

4.2.4. Magma Temperature and Oxygen Fugacity

[32] It is interesting to note that a magma temperature of 1373 ± 30 K was measured directly at Nyiragongo by Tazieff [1984]. Magma temperatures of ≥ 1370 K were also derived from crystallization experiments by [Giordano *et al.*, 2007]. Using the empirical relationship given by Mori and Notsu [1997], we can use our molar CO/CO₂ ratio to derive an estimate of the equilibrium temperature of the gas plume. A temperature of ~ 1380 K is obtained which is in excellent agreement with the previous studies and we can therefore assume that the reaction $2\text{CO} + \text{O}_2 = \text{CO}_2$ was quenched

Table 6. H₂O/CO₂, CO₂/SO₂, SO₂/HCl, and HCl/HF Molar Ratios for Volcanoes From a Variety of Tectonic Settings^a

Volcano	H ₂ O/CO ₂	CO ₂ /SO ₂	SO ₂ /HCl	HCl/HF
Divergent-plate	4.9 to 29.8	0.27 to 1.9	17.6 ^b	-
Convergent-plate	20.5 to 1633	0.49 to 21.2	0.15 to 3.3	2.5 to >39.2
Masaya ^c	27.9 to 29.0	2.5 to 2.3	1.6 to 1.7	4.5
Etna ^d	6.5	3.5	9.7	3.5
Kilauea summit	2.1	2.2	>78.0	-
Kilauea East rift zone	23.1	0.26	89.6	0.91
Nyiragongo (this study)	3.0	5.1	18.2	2.4

^a All data are from Symonds *et al.* [1994] (a compilation of quenched, restored, apparent, and estimated equilibrium compositions of 136 high-temperature gas samples) unless otherwise stated.

^b Data only available for Erta 'Ale.

^c FTIR spectroscopic data from Burton *et al.* [2000].

^d FTIR spectroscopic data from Allard and Burton [2004].

immediately after the gases were expelled from the magma. In addition, the consistency of CO/CO₂ ratios retrieved from IR spectra indicates that CO was not appreciably affected by atmospheric oxidation along the optical path. As a result we calculate oxygen fugacity (fO_2) at a temperature of 1373 K from our average CO/CO₂ ratio and standard thermodynamic data for the reaction $2CO + O_2 = 2CO_2$. The value obtained, $\log fO_2 = -9.57$, is within a quarter of a log unit below the quartz-fayalite-magnetite (QFM) buffer. This value is comparable with data presented by Gerlach [1980], who used CO/CO₂ ratios from 13 Nyiragongo gas samples to calculate fO_2 at their reported collection temperatures. Twelve of the 13 samples formed a tight fO_2 versus temperature trend that lay within a half of a log unit below the QFM buffer. The fO_2 at Nyiragongo is low when compared to values measured at convergent-plate volcanoes such as Augustine, Etna, Merapi, Momotombo, Mount St. Helens, Poas, Showa-Shinzan and Usu (fO_2 values at these volcanoes are up to two log units above the QFM buffer), and the hot spot volcano, Kīlauea (values are within a half of a log unit above the QFM buffer), but are comparable with divergent-plate volcanoes such as Ardoukoba, Erta 'Ale and Surtsey whose values lie within a half of a log unit below the QFM buffer [Symonds *et al.*, 1994].

5. Conclusion

[33] Using ground-based UV and IR spectroscopy, we successfully measured the flux of SO₂ from Nyiragongo volcano, in May/June 2005 and January 2006, and molar proportions of the gas species H₂O, CO₂, SO₂, CO, HCl, HF and OCS in the plume emitted from the lava lake in May/June 2005, January 2006 and June 2007.

[34] UV-DOAS measurements have confirmed Nyiragongo to be a significant point source of SO₂ to the free troposphere, although it is clear from comparisons with satellite-based observations that emissions have declined significantly since the period of intense degassing in 2002/2003. Combining UV-DOAS SO₂ flux data with X/SO₂ ratios measured by FTIR spectroscopy we obtain H₂O, CO₂, SO₂, CO, HCl, HF and OCS fluxes of 168, 138, 38, 3.2, 1.2, 0.3 and 0.018 kg s⁻¹, respectively, in 2005, and H₂O, CO₂, SO₂, CO, HCl and OCS fluxes of 103, 78, 23, 1.8, 0.7 and 0.011 kg s⁻¹, respectively, in 2006. These values demonstrate that Nyiragongo is a strong source of CO₂ to the atmosphere compared to other passively

degassing volcanoes but a relatively weak emitter of the halogen bearing species, HCl and HF. These observations are reflected in the comparatively low H₂O/CO₂ and high SO₂/HCl and SO₂/HF ratios that have been recorded.

[35] The composition of the plume was remarkably similar in 2005, 2006 and 2007, showing little temporal variation in proportions of CO₂, SO₂ and CO on scales of seconds, days or even between the three observation periods, spanning 24 months, despite the wide range of degassing behaviors and SO₂ emission rates that were observed. This has been explained by a system of steady state degassing where bubbles nucleate, rise and continually equilibrate with the surrounding melt as it convects. Short-term (seconds to minutes) temporal fluctuations in the SO₂-HCl-HF composition were observed and these have been attributed to shallow degassing processes.

[36] Significantly higher proportions of H₂O and SO₂ and lower proportions of CO₂ were observed compared with previous studies carried out at Nyiragongo in 1959 and 1972. These differences could be a result of long-term progressive depletion of CO₂ from a source region at depth or alternatively, the result of a different batch of magma now feeding the Nyiragongo lava lake.

[37] In conclusion, our data confirm the potential of ground-based remote-sensing techniques for quantifying and monitoring gas emissions from Nyiragongo and probing the dynamics of degassing within the conduit system. Future studies on melt inclusions to constrain the initial volatile contents of Nyiragongo magma, and work on the solubility of volatiles in the melt, are essential in order to constrain volumes of magma required to sustain the observed SO₂ fluxes and to interpret our observations on gas composition more rigorously.

Acknowledgments

[38] This work has been supported by the National Geographic Society (grant 7698-04) and by the States of Jersey Education Committee. S.A.C. also acknowledges the support of the National Science Foundation (EAR-0510185), and C.O. acknowledges support from the EU-funded Sixth Framework Programme project 18354 "NOVAC" (Network for Observation of Volcanic and Atmospheric Change). We thank Jacques Durieux, Mahinda Kasereka, Dario Tedesco, Jacques Barthelemy, Ken Sims, and all at the Goma Volcano Observatory for their logistical support and invaluable help in the field. We also thank Patrick Allard and Tobias Fischer for their helpful comments and suggestions. P. Husson (Toulouse



VAAC) kindly provided the wind speed data from the ARPEGE model.

References

- Allard, P., and M. Burton (2004), High resolution FTIR sensing of magmatic gas composition during explosive eruption of primitive Etna basalt, *Geophys. Res. Abstr.*, **6**, Abstract 06493.
- Allard, P., et al. (1991), Eruptive and diffuse emissions of CO₂ from Mount Etna, *Nature*, **351**, 387–391.
- Allard, P., et al. (2005), Spectroscopic evidence for a lava fountain driven by previously accumulated magmatic gas, *Nature*, **433**, 407–410.
- Andres, R. J., and J. W. Schmid (2001), The effects of volcanic ash on COSPEC measurements, *J. Volcanol. Geotherm. Res.*, **108**, 237–244.
- Baxter, P. J., et al. (2004), Human health and vulnerability in the Nyiragongo Volcano eruption and humanitarian crisis at Goma, Democratic Republic of Congo, *Acta Vulcanol.*, **15**(1–2), 109–114.
- Belviso, S., et al. (1986), Estimate of carbonyl sulfide (OCS) volcanic source strength deduced from OCS/CO₂ ratios in volcanic gases, *Geophys. Res. Lett.*, **13**, 133–136.
- Bluth, G. J. S., and S. A. Carn (2008), Exceptional sulphur degassing from Nyamuragira volcano, 1979–2005, *Int. J. Remote Sens.*, in press.
- Burrows, J. P., et al. (1999), Atmospheric remote-sensing reference data from GOME — 2. Temperature-dependent absorption cross sections of O₃ in the 231–794 nm range, *J. Quant. Spectrosc. Radiat. Transfer*, **61**(4), 509–517.
- Burton, M., et al. (2003), FTIR remote sensing of fractional magma degassing at Mount Etna, Sicily, in *Volcanic Degassing*, edited by C. Oppenheimer, D. M. Pyle, and J. Barclay, *Geol. Soc. Spec. Publ.*, **213**, 281–293.
- Burton, M., et al. (2007), Magmatic gas composition reveals the source depth of slug-driven Strombolian explosive activity, *Science*, **317**, 227–230.
- Burton, M. R. (1999), Remote sensing of the atmosphere using Fourier transform spectroscopy, Ph.D. dissertation, Dept. of Chemistry, Univ. of Cambridge, Cambridge, U. K.
- Burton, M. R., et al. (2000), Remote sensing of CO₂ and H₂O emission rates from Masaya volcano, Nicaragua, *Geology*, **28**, 915–918.
- Burton, M. R., et al. (2007), The role of gas percolation in quiescent degassing of persistently active basaltic volcanoes, *Earth Planet. Sci. Lett.*, **264**(1–2), 46–60.
- Carn, S. A. (2004), Eruptive and passive degassing of sulphur dioxide at Nyiragongo volcano (D. R. Congo): The 17th January 2002 eruption and its aftermath, *Acta Vulcanol.*, **15**(1–2), 75–85.
- Carn, S. A., and G. J. S. Bluth (2003), Prodigious sulfur dioxide emissions from Nyamuragira volcano, D.R. Congo, *Geophys. Res. Lett.*, **30**(23), 2211, doi:10.1029/2003GL018465.
- Carroll, M. R., and J. D. Webster (1994), Solubilities of sulphur, noble gases, nitrogen, chlorine, and fluorine in magmas, in *Volatiles in Magmas*, *Rev. Mineral.*, vol. 30, edited by M. R. Carroll, and J. R. Holloway, chap. 7, pp. 231–279, Mineral. Soc. of Am., Washington, D. C.
- Chaigneau, M., et al. (1960), Composition des gaz volcaniques du lac de lave permanent du Nyiragongo (Congo Belge), *C. R. Hebd. Seances Acad. Sci.*, **250**, 2482–2485.
- Delsemme, A. (1960), Premiere contribution a l'etude du debit d'energie du Niragongo, *Bull. Acad. R. Sci. Outre-Mer*, **6**(4), 699–707.
- Deque, M., et al. (1994), The Arpege/Ifs atmosphere model—A contribution to the French community climate modelling, *Clim. Dyn.*, **10**, 249–266.
- Durieux, J. (2003), Nyiragongo: The January 10th, 1977, eruption, *Acta Vulcanol.*, **15**(1–2), 145–147.
- Edwards, D. J., and A. Dudhia (1996), Reference Forward Model: High level algorithms definition, *ESA Doc. PO-MA-OXF-GS-0004*, Eur. Space Agency, Paris.
- Francis, P., et al. (1998), Remote measurements of volcanic gas compositions by solar occultation spectroscopy, *Nature*, **396**, 567–570.
- Galle, B., et al. (2002), A miniaturised ultraviolet spectrometer for remote sensing of SO₂ fluxes: A new tool for volcano surveillance, *J. Volcanol. Geotherm. Res.*, **119**, 241–254.
- Galle, B., et al. (2005), Gas emissions from Nyiragongo, D.R. of Congo, measured by UV mini-DOAS spectroscopy, *Geophys. Res. Abstr.*, **7**, Abstract 08332.
- Gerlach, T. M. (1980), Chemical characteristics of the volcanic gases from Nyiragongo lava lake and the generation of CH₄-rich fluid inclusions in alkaline rocks, *J. Volcanol. Geotherm. Res.*, **8**, 177–189.
- Gerlach, T. M. (1982), Interpretation of volcanic gas data from theoleiitic and alkaline mafic lavas, *Bull. Volcanol.*, **45**, 235–244.
- Giggenbach, W. F. (1992), Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin, *Earth Planet. Sci. Lett.*, **113**, 495–510.
- Giordano, D., et al. (2007), Thermo-rheological magma control on the impact of highly fluid lava flows at Mt. Nyiragongo, *Geophys. Res. Lett.*, **34**, L06301, doi:10.1029/2006GL028459.
- Global Volcanism Network (GVN) (1994a), Nyiragongo, *Bull. Global Volcanism Network*, **19**, 7.
- GVN (1994b), Nyiragongo, *Bull. Global Volcanism Network*, **19**(6), Smithsonian Inst., Washington, D. C.
- GVN (1996), Nyiragongo, *Bull. Global Volcanism Network*, **21**(10), Smithsonian Inst., Washington, D. C.
- GVN (2001), Nyiragongo, *Bull. Global Volcanism Network*, **26**(3), Smithsonian Inst., Washington, D. C.
- GVN (2002a), Nyiragongo, *Bull. Global Volcanism Network*, **27**(5), Smithsonian Inst., Washington, D. C.
- GVN (2002b), Nyiragongo, *Bull. Global Volcanism Network*, **27**(10), Smithsonian Inst., Washington, D. C.
- Horrocks, L., et al. (1999), Stable gas plume composition measured by OP-FTIR spectroscopy at Masaya Volcano, Nicaragua, 1998–1999, *Geophys. Res. Lett.*, **26**(23), 3497–3500.
- Jaupart, C., and S. Vergnolle (1988), Laboratory models of Hawaiian and Strombolian eruptions, *Nature*, **331**, 58–60.
- Jaupart, C., and S. Vergnolle (1989), The generation and collapse of a foam layer at the roof of a basaltic magma chamber, *J. Fluid Mech.*, **203**, 347–380.
- Komorowski, J.-C., et al. (2004), The January 2002 flank eruption of Nyiragongo volcano (Democratic Republic of Congo): Chronology, evidence for a tectonic rift trigger, and impact of lava flows on the city of Goma, *Acta Vulcanol.*, **15**(1–2), 27–61.
- Krafft, M., and K. Krafft (1983), The reappearance of the lava lake in the crater of Nyiragongo volcano from June to September 1982 (Kivu-Zaire)—History, behavior, outputs and volcanic risks, *C. R. Acad. Sci., Ser. II*, **296**, 797–802.



- Kraus, S. (2006), *DOASIS—A Framework Design for DOAS*, 161 pp., Shaker, Manheim, Germany.
- Krotkov, N. A., et al. (2006), Band residual difference algorithm for retrieval of SO₂ from the aura Ozone Monitoring Instrument (OMI), *IEEE Trans. Geosci. Remote Sens.*, *44*, 1259–1266.
- Le Guern, F. (1987), Mechanism of energy transfer in the lava lake of Niragongo (Zaire), 1959–1977, *J. Volcanol. Geotherm. Res.*, *31*, 17–31.
- Marquardt, D. W. (1963), An algorithm for least squares estimation of nonlinear parameters, *J. Soc. Ind. Appl. Math.*, *11*, 431–441.
- Mather, T. A., et al. (2004), Characterization and evolution of tropospheric plumes from Lascar and Villarrica volcanoes, Chile, *J. Geophys. Res.*, *109*, D21303, doi:10.1029/2004JD004934.
- Mather, T. A., et al. (2006), A reassessment of current volcanic emissions from the Central American arc with specific examples from Nicaragua, *J. Volcanol. Geotherm. Res.*, *149*, 297–311.
- Mori, T., and K. Notsu (1997), Remote CO, COS, CO₂, SO₂, HCl detection and temperature estimation of volcanic gas, *Geophys. Res. Lett.*, *24*, 2047–2050.
- Oppenheimer, C., et al. (1998), Depletion rates of sulfur dioxide in tropospheric volcanic plumes, *Geophys. Res. Lett.*, *25*, 2671–2674.
- Oppenheimer, C., et al. (2002), Open-path Fourier transform spectroscopy of gas emissions from Oldoinyo Lengai volcano, Tanzania, *Opt. Lasers Eng.*, *37*, 203–214.
- Oppenheimer, C., et al. (2004), NO₂ emissions from agricultural burning in Sao Paulo, Brazil, *Environ. Sci. Technol.*, *38*, 4557–4561.
- Oppenheimer, C., et al. (2006), Rapid FTIR sensing of volcanic gases released by Strombolian explosions at Yasur volcano, Vanuatu, *Appl. Phys. B*, *85*, 453–460.
- Parfitt, E. A. (2004), A discussion of the mechanisms of explosive basaltic eruptions, *J. Volcanol. Geotherm. Res.*, *134*, 77–107.
- Parfitt, E. A., and L. Wilson (1995), Explosive volcanic eruptions. 9. The transition between Hawaiian-style lava fountaining and strombolian explosive activity, *Geophys. J. Int.*, *121*, 226–232.
- Platt, U. (1994), Differential optical absorption spectroscopy (DOAS), in *Air Monitoring by Spectroscopic Techniques*, *Chem. Anal.*, vol. 127, edited by M. W. Sigrist, pp. 27–84, John Wiley, New York.
- Rodgers, C. D. (1976), Retrieval of atmospheric temperature and composition from remote measurements of thermal radiation, *Rev. Geophys.*, *14*, 609–624.
- Rothman, L. S., et al. (2005), The HITRAN 2004 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transfer*, *96*, 139–204.
- Rufus, J., et al. (2003), High-resolution photoabsorption cross section measurements of SO₂, 2: 220 to 325 nm at 295 K, *J. Geophys. Res.*, *108*(E2), 5011, doi:10.1029/2002JE001931.
- Sahama, T. G. (1962), Petrology of Mt. Nyiragongo: A review, *Trans. Edinburgh Geol. Soc.*, *19*, 1–28.
- Sahama, T. G. (1973), Evolution of Nyiragongo magma, *J. Petrol.*, *14*, 33–48.
- Sawyer, G. M., and M. R. Burton (2006), Effects of a volcanic plume on thermal imaging data, *Geophys. Res. Lett.*, *33*, L14311, doi:10.1029/2005GL025320.
- Scientific Event Alert Network (SEAN) (1977a), Nyiragongo, *Sci. Event Alert Network Bull.*, *2*(1), Smithsonian Inst., Washington, D. C.
- SEAN (1977b), Nyiragongo, *Sci. Event Alert Network Bull.*, *2*(3), Smithsonian Inst., Washington, D. C.
- Seinfeld, J. H., and S. N. Pandis (2006), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd ed., 1203 pp., John Wiley, New York.
- Shinohara, H., and J. B. Witter (2005), Volcanic gases emitted during mild Strombolian activity of Villarrica volcano, Chile, *Geophys. Res. Lett.*, *32*, L20308, doi:10.1029/2005GL024131.
- Stoiber, R. E., et al. (1983), Use of the correlation spectrometer at volcanoes, in *Forecasting Volcanic Events*, edited by H. Tazieff, and J.-C. Sabroux, pp. 425–444, Elsevier, Amsterdam.
- Symonds, R. B., et al. (1994), Volcanic-gas studies: Methods, results, and applications, in *Volatiles in Magmas*, *Rev. Mineral.*, vol. 30, edited by M. R. Carroll, and J. R. Holloway, chap. 7, pp. 1–66, Mineral. Soc. of Am., Washington, D. C.
- Tazieff, H. (1977), An exceptional eruption: Mt. Nyiragongo, January 10th, 1977, *Bull. Volcanol.*, *40*, 189–200.
- Tazieff, H. (1979), *Nyiragongo, the Forbidden Volcano*, 287 pp., Barron's, London.
- Tazieff, H. (1984), Mt Niragongo—Renewed activity of the lava lake, *J. Volcanol. Geotherm. Res.*, *20*, 267–280.
- Tazieff, H. (1994), Permanent lava lakes—Observed facts and induced mechanisms, *J. Volcanol. Geotherm. Res.*, *63*, 3–11.
- Tedesco, D. (1995), Report on the Virunga volcanic region and on the related volcanic risk, United Nations internal report, Dept. of Humanitarian Affairs, Geneva.
- Wardell, L. J., et al. (2004), Carbon dioxide and carbon monoxide emission rates from an alkaline intra-plate volcano: Mt. Erebus, Antarctica, *J. Volcanol. Geotherm. Res.*, *131*, 109–121.
- Weibring, P., et al. (2002), Optical monitoring of volcanic sulphur dioxide emissions—Comparison between four different remote sensing spectroscopic techniques, *Opt. Lasers Eng.*, *37*, 267–284.