Steam and gas emission rate from La Soufriere volcano, Guadeloupe (Lesser Antilles): Implications for the magmatic supply during degassing unrest

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ABSTRACT

Since its last magmatic eruption in 1530 AD, La Soufrière andesitic volcano in Guadeloupe has displayed intense hydrothermal activity and six phreatic eruptive crises. Here we report on the first direct quantification of gas plume emissions from its summit vents, which gradually intensified during the past 20 years. Gas fluxes were determined in March 2006 and March 2012 by measuring the horizontal and vertical distributions of volcanic gas concentrations in the air-diluted plume and scaling to the speed of plume transport. Fluxes in 2006 combine real-time measurements of volcanic H₂S concentrations and plume parameters with the composition of the hot (108.5 °C) fumarolic fluid at exit. Fluxes in 2012 result from MultiGAS analysis of H₂S, H₂O, CO₂, SO₂ and H₂ concentrations, combined with thermal imaging of the plume geometry and dynamics. Measurements were not only focused on the most active South crater (SC) vent, but also targeted Tarissan crater and other reactivating vents. We first demonstrate that all vents are fed by a common H₂O-rich (97–98 mol%) fluid end-member, emitted almost unmodified at SC but affected by secondary shallow alterations at other vents. Daily fluxes in 2012 averaged 200 tons of H₂O, 15 tons of CO₂, ~4 tons of H₂S and 1 ton of HCl, increased by a factor ~3 compared to 2006. Even though modest, such fluxes make La Soufrière the second most important volcanic gas emitter in the Lesser Antilles arc, after Soufrière Hills of Montserrat. Taking account of other hydrothermal manifestations (hot springs and diffuse soil degassing), the summit fumarolic activity is shown to contribute most of the bulk volatile and heat budget of the volcano. The hydrothermal heat output (8 MW) exceeds by orders of magnitude the contemporaneous seismic energy release. Isotopic evidences support that La Soufrière hydrothermal emissions are sustained by a variable but continuous heat and gas supply from a magma reservoir confined at 6–7 km depth. By using petro-geochemical data for La Soufrière magma(s) and their dissolved volatile content, and assuming a magmatic derivation of sulfur, we estimate that the volcanic gas fluxes measured in 2012 could result from the underground release of magmatic gas exsolved from ~1400 m³ d^{−1} of basaltic melt feeding the system at depth. We recommend that fumarolic gas flux at La Soufrière becomes regularly measured in the future in order to carefully monitor the temporal evolution of that magmatic supply.

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1. Introduction

Increasing gas emission and compositional changes in fumarolic exhalations are common signals of unrest or even precursors of forthcoming eruption at dormant volcanoes in hydrothermal stage of activity (e.g. Giggensch and Sheppard, 1989; Symonds et al., 1994, 1996). Deciphering the actual significance of these signals is thus important

to discriminate between pure physical changes in the hydrothermal system regime (e.g. sealing, overpressuring) and evolution due to degassing of uprising magma prone to erupt. Both mechanisms can trigger phreatic eruptions of similar style but with highly contrasted implications. While monitoring fumarolic gas compositions is routinely operated on a number of dormant volcanoes worldwide, quantifying the total gas discharge sustained by fumarolic activity – one key information upon the evolution of volatile and heat budgets – is not trivial. On volcanoes with sustained open-vent magma degassing or/and hosting high-temperature (>400 °C) fumarolic systems, gas discharges are accurately quantified using remote UV spectroscopy of plume

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emissions of sulfur dioxide (e.g., Oppenheimer, 2010). The fluxes of other gas compounds are then calculated from knowledge of fumarole or plume compositions (e.g., Allard et al., 1994). Instead, this approach is prevented at less active (<200–300 °C) degassing systems that emit little SO₂ and predominantly H₂S, this latter being far more difficult to detect optically in volcanic plumes (O'Dwyer et al., 2003). Other

techniques for the remote flux sensing of H₂O and CO₂, the two main volcanic gas species, are still in the developing stage (e.g. Fiorani et al., 2011; Schwandner et al., 2012). Alternative possibilities are in situ flux measurement using airborne gas plume profiling (Gerlach et al., 1999) or ground-based eddy gas profiling (Todesco et al., 2003), but these are often hampered by the weakness of air-diluted fumarolic

Fig. 1. Locations of (a) Guadeloupe island in the Lesser Antilles arc and (b) La Soufrière volcano in the southern part of Basse Terre island. (c) Picture of La Soufrière summit lava dome, extruded during the last eruption in 1530 AD, with its visible summit gas plume in March 2012. (d) Digital topographic map of the lava dome showing its main fractures and the active summit fumarolic vents investigated in this study (South Crater: SC; Tarissan crater: TAS; Gouffre 1956: GF56; Lacroix fracture: LC).

emissions, topographic obstacles and/or too high costs. Therefore, quantitative gas flux evaluation at volcanoes with low-temperature fumarolic activity is scarcely achieved, which deserves new approaches with adequate measuring tools. This is of outmost importance since most dormant volcanic systems worldwide fall in this second category.

One of such systems is La Soufrière volcano in Guadeloupe, in the Lesser Antilles arc (Fig. 1a). La Soufrière is the youngest volcanic relief topping a far larger ($\sim 16 \text{ km}^3$) and long-lived ($>200 \text{ ka}$; Samper et al., 2007) active volcanic complex, the Grande Découverte–Soufrière composite volcano, located in the southern part of Basse Terre island (Boudon et al., 1989; Komorowski et al., 2005; Fig. 1b). It consists of an $\sim 0.05 \text{ km}^3$ lava dome that was emplaced during the final stage of the last magmatic eruption in 1530 AD (Boudon et al., 2008). Since then, intense hydrothermal activity (fumaroles, solfataras, hot springs) has persisted on and around the lava dome, and six series of phreatic eruptions happened, the most recent one in 1976–1977 (Le Guern et al., 1980; Feuillard et al., 1983). This activity represents the surface expression of a well-developed hydrothermal system (Le Guern et al., 1980; Zlotnicki et al., 1992; Brombach et al., 2000; Villemant et al., 2005) that receives heat and gas from a magma reservoir probably confined at 6–7 km depth beneath the summit (Hirn and Michel, 1979; Pozzi et al., 1979; Semet et al., 1981; Feuillard et al., 1983; Poussineau, 2005). Isotopic investigations actually demonstrate a persistent contribution of magma-derived volatiles to La Soufrière fumarolic gas emissions and thermal waters (Allard et al., 1982; Allard, 1983, 2006; Van Soest et al., 1998; Pedroni et al., 1999; Li et al., 2012; Ruzié et al., 2012, 2013; Jean-Baptiste et al., 2013). Accordingly, the volcano is closely monitored by the local Volcanological and Seismological Observatory (OVSG-IPGP). In particular, its fumarolic gases and thermal springs are routinely sampled and analysed in complement to seismic and geodetic survey (OVSG-IPGP reports, 1992–2012).

Since 1992 a new phase of fumarolic unrest has developed on top of La Soufrière lava dome, in concomitance with renewed shallow seismicity, generating extremely acidic ($\text{Cl} > 0.1 \text{ mol}\%$) chlorine-enriched gas emissions since 1998 (OVSG-IPGP reports, 1992–2012; Villemant et al., 2005; Bernard et al., 2006). Fumarolic emissions have become intense enough to generate a volcanic plume, visible from several kilometres distance during clear days, whose acidity destroys the vegetation (Fig. 1c). This degassing unrest, with progressive reactivation of several summit vents, is still increasing and raises concern about the future evolution of the volcano. However, because the fumarolic fluids contain few SO_2 (e.g. OVSG-IPGP reports, 1992–2012; Brombach et al., 2000; Bernard et al., 2006; this work) and the volcanic plume remains too weak to be resolved with remote/airborne techniques, no quantitative gas flux monitoring has ever been set up to complement volcanic hazard assessment. Up to now, only a few indirect attempts were made to assess the fumarolic gas discharge using either velocity measurements at vents or plume modelling from thermal imagery (Beauducel et al., submitted for publication).

Here we report on the first direct quantification of the fumarolic gas discharge from La Soufrière based on real-time gas measurements performed in March 2006 then March 2012. Gas fluxes were obtained by measuring with portable instruments the horizontal and vertical distributions of gas concentrations in cross-sections and along the blowing axis of the volcanic plume, subsequently scaled to the plume transport speed. The hot fumarolic fluid was simultaneously sampled and analysed. Our 2012 dataset, in particular, provides the bulk composition (H_2O , CO_2 , H_2S , SO_2 and H_2) of plume emissions from the different vents currently active on top of La Soufrière, measured with a MultiGAS sensor (Aiuppa et al., 2005a), and accurate estimate of the present-day bulk volcanic fluxes based on simultaneous thermal infrared imaging of the plume structure and dynamics. Our results are then discussed in terms of bulk volatile and heat budget, magma degassing supply, and interaction between magma-derived fluids and the hydrothermal system during the current degassing unrest.

2. La Soufrière volcano

La Soufrière (Fig. 1) is an $\sim 1470 \text{ m}$ -high lava dome made up of crystal-rich andesite ($\sim 56\% \text{ SiO}_2$) that extruded in former Amic crater at the end of the 1530 AD eruption (Boudon et al., 2008). The eruption initiated with a flank collapse and a sub-Plinian phase accompanied by scoria fallout and pyroclastic flows that involved smaller amounts of more evolved felsic ($57\text{--}61\% \text{ SiO}_2$) andesite (Boudon et al., 2008). This eruption is the last major magmatic episode of the so-called La Soufrière activity phase (11,500 B.P. to present) of the Grande Découverte–Soufrière volcanic complex, marked by an alternation of dome-building eruptions, phreatic eruptions, and edifice collapse events leading to emplacement of $0.1\text{--}0.5 \text{ km}^3$ debris avalanches on the S–SW slopes of the edifice (Boudon et al., 1989; Komorowski et al., 2005). Petro-geochemical data show that the Grande Découverte–Soufrière composite volcano has been fed by a long-lived ($>30 \text{ ka}$; Touboul et al., 2007) andesitic magma reservoir, repeatedly replenished from depth with basalt, whose products belong to the same differentiation (crystal fractionation) series as other volcanics from the Basse Terre axial Volcanic Chain and the Mts. Caraïbes basaltic massif to the south (Semet et al., 1981; Boudon et al., 2008). The roof of this reservoir is inferred at about 6–7 km depth below the summit, or $\sim 5 \pm 0.5 \text{ km}$ below sea level, from both seismic and petrologic data (Hirn and Michel, 1979; Pozzi et al., 1979; Feuillard et al., 1983; Poussineau, 2005; Boudon et al., 2008). Recent seismic tomography of the underlying arc crust (Kopp et al., 2011) shows that such a depth corresponds approximately to the interface between the upper layer of the arc crust, made of volcanoclastic sediments and fractured volcanic rocks, and an $\sim 10 \text{ km}$ thick middle layer composed of denser volcanic/intrusive bodies of felsic to intermediate composition.

The repose period since the 1530 AD eruption has been punctuated by six phreatic eruption phases in 1690, 1797–98, 1812, 1836–37, 1956 and 1976–77. The 1976–1977 eruptive phase provoked the evacuation of 73,000 people for about four months from the southern part of Basse Terre island (Le Guern et al., 1980; Feuillard et al., 1983). Its source mechanism has been the matter of great controversy during the events and still remains debated 38 years later: some authors interpreted this phreatic episode as a failed (still-born) magmatic eruption (Feuillard et al., 1983), possibly involving small magma intrusion that stopped a few kilometres from the surface (Villemant et al., 2005; Boichu et al., 2011), while others argued that it could have resulted from simple destabilization of the hydrothermal system due to either self-sealing pressurization (Le Guern et al., 1980; Zlotnicki et al., 1992) or, instead, depressurization due to tectonic earthquake fracturing (Allard, 2006). Whatever the truth, La Soufrière volcano constitutes a permanent threat for increasingly inhabited areas on its southern slopes, where the towns of Saint-Claude (10,000) and Basse Terre (40,000) stand only 5 and 10 km from its summit. In particular, pervasive hydrothermal alteration of the lava dome and its highly fractured state enhance the risk of pure gravitational dome failure (Komorowski et al., 2005) that could directly not only affect the surroundings but also decompress the hydrothermal system.

After the 1976–77 events La Soufrière fumarolic activity gradually declined both in intensity and spatial extent: fumarolic manifestations gradually vanished around the lava dome, except along the NNW–SSE regional Ty fault (Fig. 1c), and weakly persisted along previously formed radial fractures of the dome (Fig. 1d). A decrease of both chlorine and sulfate was simultaneously recorded in thermal springs surrounding the lava dome (Bigot and Hammouya, 1987). In 1992, however, fumarolic activity started to intensify again on top of the dome, especially at the ‘Southern Crater’ fracture vent (SC, Fig. 1d), in coincidence with renewed seismicity. From a gas survey in 1997, Brombach et al. (2000) inferred that the H_2O -dominated fumaroles ($T \sim 93\text{--}95^\circ \text{C}$), with H_2S as the main S species and no detectable SO_2 and HCl , were sourced by boiling of $\sim 260^\circ \text{C}$ aqueous solutions of the underlying hydrothermal system. Similar temperatures had been inferred from clay

mineral assemblages present in ash particles emitted during the 1976 eruptive events (Feuillard et al., 1983). But the degassing activity further intensified in 1998, with increasing temperature (~ 105 – 110 °C) and the abrupt appearance of HCl and some SO₂ in SC fumaroles, suggesting that the system was possibly becoming more magmatic in nature (Bernard et al., 2006). A persistent magmatic gas supply to La Soufrière hydrothermal activity is actually demonstrated by the magmatic isotopic signature of chlorine in thermal springs (Li et al., 2012) and by the presence of MORB-type mantle-derived helium ($^3\text{He}/^4\text{He} = 8.2 \pm 0.2$ Ra; Allard et al., 1982; Allard, 1983; Van Soest et al., 1998; Pedroni et al., 1999; Ruzié et al., 2012, 2013; Jean-Baptiste et al., 2013, submitted for publication) and magma-derived carbon dioxide ($\delta^{13}\text{C} = -3.2 \pm 0.6\text{‰}$; Allard et al., 1983; Javoy et al., 1986; Allard, 2006; Ruzié et al., 2013) in gases emitted over the past 35 years. Between 2000 and 2002 the summit fumarolic field expanded, with reactivation of the Tarissan (TAS) and Napoléon (NAP) craters (Fig. 1d). By the time of our March 2006 survey the South Crater (SC) was the main active vent, but in March 2012 degassing had increased at both SC and TAS. Milder but renewed gas release was also occurring at spots along the Gouffre 1956 (GF56; Fig. 1d), formed during the 1956 phreatic eruption, and at Lacroix fracture (LC).

3. Experimental procedures

3.1. Fumarolic gas sampling and analysis

Since the onset of current degassing unrest at La Soufrière, fumarolic gases have been routinely sampled at SC vent (Fig. 1d) and analysed by the volcano Observatory (OVSG-IPGP reports, 1992–2012). This most active fracture vent is the main source of the volcanic plume and the only one accessible for hot gas sampling. In March 2006 and March 2012 SC fumarolic fluid was issuing at 108.5 ° and 107.6 °C, superheated with respect to the temperature of boiling water (96.7 °C) at the elevation. A 3-m long insulated pipe introduced in the vent was used to drain the fluid into pre-evacuated glass bottles, filled with either P₂O₅ desiccant or a NaOH solution, that were connected either directly or in series behind two glass condensers cooled with acetone. The high gas flow rate allowed efficient flushing of the overall sampling line and separate collection of the condensed steam and the ‘dry’ gas phase. In March 2006 we determined in situ the steam/gas ratio of the fumarolic fluid by repeatedly comparing the collected amount of condensed steam with the amount of ‘dry’ gas simultaneously pumped into a 250 ml syringe, with a 3-way stopcock, positioned at the open end of the sampling line. In 2012 the H₂O/gas ratio of the fumarolic fluid was inferred from MultiGAS analysis of near-vent SC volcanic plume (see below).

Gas analyses were performed soon after sampling at the volcano Observatory using a quadrupole mass spectrometer (Balzers Prisma QMS 200). The instrument is configured for routine analysis of CO₂, H₂S, SO₂, H₂, CO, CH₄, N₂, O₂, He and Ar, with accurate de-convolution of mass interferences (OVSG-IPGP reports). Concentrations are obtained by calibration with a set of standard gas mixtures and analytical uncertainties (± 1 – 5% for the main components to ± 10 – 20% for minor components) are determined through Monte-Carlo statistical treatment. H₂O is determined by gravimetric weighing. The HCl content of the fumarolic fluid is given by the Cl[−] content (± 3 – 5%) of steam condensates, routinely measured with ion (Dionex) chromatography at the Observatory (OVSG-IPGP reports). The bulk chemical composition of SC fumarolic fluid measured in March 2006 and March 2012 is reported in Table 1.

3.2. Volcanic plume measurements

3.2.1. 2006 measurements

Our measurements on 27 March 2006 benefited from excellent, rare weather conditions on top of La Soufrière, where the rainfall rate reaches ~ 8 – 10 m per year and humidity is commonly close to 100%

Table 1

Molar composition of La Soufrière's South Crater (SC) fumarolic fluid in March 2006 and March 2012.

	27/03/2006	07/03/2012
T°C	108.5	107.6
H ₂ O (mol%)	97.8	96.6
pH	0.8	0.93
HCl	0.3	0.37
'Dry' gas (mol%)	1.9	3.0
CO ₂	66.4	67.3
H ₂ S	30.8	29.2
SO ₂	0.62	0.31
H ₂	0.79	0.42
CH ₄	0.08	0.19
CO	0.007	0.003
N ₂	1.01	2.52
O ₂	0.26	0.04
He ppm	5.4	6.2
N ₂ /Ar	73	78
H ₂ O/H ₂ S	144	100
CO ₂ /H ₂ S	2.16	2.30
SO ₂ /H ₂ S	0.02	0.01
HCl/H ₂ S	0.48	0.38
$^3\text{He}/^4\text{He}$ (R/R _a)	8.35	7.90
CO ₂ / ^3He	$1.1\text{E}+10$	$1.0\text{E}+10$

Chemical analyses performed with quadrupole mass spectrometry and ion chromatography (CI) at the OVSG volcano observatory (see Section 3.1). H₂O content (and steam/gas ratio) was determined directly in the field in 2006 and indirectly from MultiGAS analysis of SC plume in 2012 (Section 4.1 and Table 2). Helium content and the $^3\text{He}/^4\text{He}$ ratio (corrected for neon-related air contamination) were determined at LSCE (Saclay, France) using a MAP-215-50 mass spectrometer (Jean-Baptiste et al., 2013, submitted for publication).

(e.g. Chaperon et al., 1985). Regular control with a hand-held meteorological sensor showed a stable ambient pressure of 858.5 hPa and limited variations of air temperature (19 to 16 °C) and relative humidity (48 to 60%) during our measurements. E–W trade winds were blowing at a very constant mean speed of 3.6 ± 0.2 m s^{−1}. Such weather conditions allowed accurate viewing and analysis of the volcanic plume from SC vent (Fig. 2a).

Since H₂S is absent in normal atmosphere and the main sulfur-bearing species in La Soufrière gases (OVSG-IPGP reports, 1992–2012; Brombach et al., 2000; Bernard et al., 2006; this work), we used it as specific marker of the volcanic plume emission. H₂S concentrations (ppmv) in the air-diluted plume were measured in real time using a portable electrochemical sensor (Membrapor H₂S/S-type: 0–50 ppmv range, $\pm 2\%$ accuracy; Aiuppa et al., 2005a), previously calibrated in laboratory. Horizontal and vertical concentration profiles were measured during a traverse orthogonal to the plume direction performed 5 m downwind SC vent (Fig. 3a–b), then during a profile along the plume axis at 2 to 55 m distance range from the vent (Fig. 3c–d). At each point H₂S concentration was continuously measured for 1–3 min in order to obtain a time-averaged value smoothed for short-lived fluctuations in wind turbulence and air dilution of the plume. Horizontal profiling was made with steps of 2.5 to 5 m, depending on topography, and vertical concentration gradients were measured at intervals of 25–50 cm between the ground and 2.3 m height (the maximum height of visible plume). GPS site coordinates, wind speed (± 0.1 m s^{−1}), the plume's temperature (± 0.1 °C) and relative humidity (RH, $\pm 0.1\%$) were simultaneously recorded at each point. RH values are converted into water vapour contents (in g m^{−3}) from the H₂O partial pressure at corresponding temperature, $P_{\text{H}_2\text{O}} = P_s \cdot \text{RH}/100$, where the vapour saturation pressure $P_s = 610.78 \cdot \exp[17.2694 \cdot t/(t + 238.3)]$. As discussed thereafter, the volcanic flux of H₂S is determined by integrating the horizontal and vertical distributions of H₂S concentrations within the volcanic plume and then scaling to the wind speed.

3.2.2. 2012 measurements

Our measurements on top of La Soufrière were performed on 5–7 March 2012 under more unstable weather conditions, with ambient

Fig. 2. Photos of South Crater (SC) vent in (a) March 2006 and (b) March 2012, and (c) of Tarissan crater (TAS) in March 2012 (P. Allard).

pressure of 845 hPa, temperature of 14–16 °C, relative humidity of ~85%, and measured wind speed varying from 27 to 6 m s⁻¹ from day to day. Our key improvement during that survey was to measure simultaneously the within-plume concentrations of both H₂S, H₂O, CO₂, SO₂ and H₂ with a portable INGV-type MultiGAS analyser (a recent description of the instrument's setup and performance can be found in Aiuppa et al., 2011, 2012). Since its advent (Aiuppa et al., 2005a,b; Shinohara, 2005), this custom-made gas sensor box has become a widely used, robust tool for volcanic gas studies and monitoring (see Aiuppa et al., 2011; Roberts et al., 2012 for an updated list of references). On La Soufrière we used two light (<3 kg) MultiGAS instruments which permit high-rate (0.5 Hz) real-time detection of H₂O and CO₂ with NDIR spectroscopy and of SO₂, H₂S and H₂ with electrochemical sensors (Aiuppa et al., 2012). The precision on concentrations is typically ±5–10%.

The instruments, carried in backpacks, were operated in the walking traverse mode, with their flexible tubing inlet being positioned so as to suck plume/background air from the desired height above the ground.

Measurements performed at the different vents active on La Soufrière lava dome (Fig. 1d) allowed us to characterise the compositional differences of their gas emissions (Table 2) and to compare them with the fumarolic fluid simultaneously sampled at SC crater (Table 1). For gas flux quantification we measured the air-diluted volcanic plumes from both SC and TAS craters (Fig. 2b,c), the two most active vents. Acquiring gas concentration data at 0.5 Hz and simultaneous GPS positioning, the MultiGAS had the required temporal/spatial resolution to map the chemical heterogeneity of the volcanic plumes. We first performed air background measurements (upwind the active vents) then in-plume concentration measurements (Fig. 1d) during repeated orthogonal (A–D in Fig. 4a,b) and co-axial (X–Y in Fig. 4a,c) traverses relative to the westerly plume transport direction, at distances of 0 to ~60 m of each vent. We also checked the vertical distribution of gas concentrations between 0 and 3.5 m above the ground. As a whole, H₂O, CO₂, SO₂, H₂S and H₂ concentrations were determined at >5000 positions and stored in the on-board memory. With respect to our March 2006 survey, we thus obtained a far larger sampling grid and for five gas species simultaneously. Bernard et al. (2006) had previously performed near-vent plume measurements on La Soufrière with a portable analyser but only along co-axial profiles, at a low time resolution (0.017 Hz), and without any gas flux assessment. Instead, here we combine our results for both orthogonal and axial gas concentration profiles with the wind speed to derive accurate constraints on the fumarolic gas discharge in 2012.

The plume's thickness and transport velocity were additionally determined from infrared thermal imaging, using an Infratec model VarioCAM HR head 410 camera. This camera works with uncooled microbolometer sensors in the infrared range 7.5–14 μm, at <0.08 K sensitivity in the –40 to 120 °C temperature range, and produces 384 × 288 pixel images with a 15° × 12° optical lens. The system is able to acquire temperature images at 1 Hz sampling or to make screenshot movies at 25 frame/s rate with fixed temperature colour-map. We positioned the camera a few tens of metres away from SC and TAS vents, looking plumes laterally, and we recorded short movies in the same time as MultiGAS measurements. We repeatedly considered 2 s-long movies, from which we extracted 50 frames and then computed a grid of velocity vectors for each couple of images using a particle image velocimetry (PIV) algorithm (Mori and Chang, 2003). The camera's small shakings due to wind were corrected using vectors on the ground part of each image.

3.3. Soil gas flux measurements

In addition to fumarolic emissions, intense diffuse soil degassing has been recognized at the southeastern base of La Soufrière lava dome (Allard et al., 1998), in a hydrothermal area aligned on the Ty fault volcano-tectonic structure that cuts the dome (Fig. 1). In March 2006 we re-determined the CO₂ concentrations (±3%, ADC-LFG20 portable infrared spectrometer) and temperatures at 30–70 cm depth in the ground in this area, along a 110 m long profile crossing the Ty fault (Citerne road), and measured for the first time the CO₂ fluxes from the volcanic ground. CO₂ fluxes (±5–7%) were measured at the soil interface (and corrected for ambient pressure) using a West Systems accumulation chamber coupled to a previously calibrated Dräger infrared spectrometer, as previously described by Chiodini et al. (1998). Further CO₂ flux investigations were realized on the lava dome itself, along the walking paths circling the dome (Sentier des Dames and Col de l'Echelle) and, punctually, near SC vent on top of the dome. Most of the lava dome being covered with abundant vegetation, a volcanic flux anomaly was considered to be significant when as much as three times the measured biogenic CO₂ flux background. The results are discussed in Section 5.3 and depicted in Fig. 9.

Fig. 3. H₂S concentrations in SC volcanic plume in March 2006. Time-averaged temperature (°C) and concentrations of H₂S (ppmv, $\pm 3\%$) and H₂O (g m⁻³, $\pm 5\%$) in the core (half thickness) of the plume (a) during an orthogonal traverse at 5 m downwind SC vent and (c) along the blowing plume axis at 2 to 55 m distance from the vent. Vertical bars for H₂S indicate the measured concentration range at each point. SCN: South crater north; SCS: South crater south. Modelled (Surfer kriging) 2D distribution of H₂S (b) within the vertical plume cross section and (d) along the horizontal blowing direction during plume dilution and transport. See text for details and discussion.

4. Results

4.1. Chemical composition of La Soufrière hot fumarolic fluid

Table 1 shows the molar composition of the fumarolic fluid directly sampled from SC vent in March 2006 and March 2012. The steam/gas volume ratio of 45 (i.e., 45 litres of steam for one litre of gas) measured

in March 2006 highlights the water-rich composition (97.8 mol%) of La Soufrière fumarolic fluids (Le Guern et al., 1980; Brombach et al., 2000; Bagnato et al., 2009). Although not directly measured in March 2012, a comparable water content of 96.6 ± 0.5 mol% is inferred from our MultiGAS data for SC volcanic plume (see Section 4.3 and Table 2). HCl ranges from 0.3 to 0.4 mol% of the bulk fluid, accounting for the high acidity of the fumarolic emissions. For the sake of comparison, the

Table 2

Molar ratios and bulk composition of gas plume exhalations from active vents at La Soufrière in March 2012, as measured with MultiGAS.

Date	Site	H ₂ O/H ₂ S	CO ₂ /H ₂ S	SO ₂ /H ₂ S	H ₂ /H ₂ S	H ₂ O/CO ₂	H ₂ O%	CO ₂ %	H ₂ S%	SO ₂ %	H ₂ %
05/03/2012 am	Southern crater	108	2.2	0.040	0.013	49.4	97.1	2.0	0.9	0.036	0.012
05/03/2012 pm	Southern crater	88	2.7	0.040	nd	32.8	95.9	2.9	1.1	0.044	nd
07/03/2012 am	Southern crater	99	2.7	0.036	0.018	36.8	96.4	2.6	1.0	0.035	0.018
07/03/2012 pm	Southern crater	106	2.4	0.025	nd	44.5	96.9	2.2	0.9	0.023	nd
07/03/2012 am	Gouffre 1956	87	2.8	0.044	nd	31.7	95.8	3.0	1.1	0.049	nd
07/03/2012 am	Lacroix inf vent	168	2.8	0.016	nd	59.4	97.8	1.6	0.6	0.009	nd
07/03/2012 am	Lacroix sup vent	247	6.0	0.025	nd	40.9	97.2	2.4	0.4	0.010	nd
07/03/2012 pm	Lacroix sup vent	260	6.5	0.029	nd	39.9	97.2	2.4	0.4	0.011	nd
05/03/2012 am	Tarissan crater	263	4.8	n.d	0.010	54.7	97.8	1.8	0.4	nd	0.004
05/03/2012 pm	Tarissan crater	147	4.2	n.d	nd	34.9	96.6	2.8	0.7	nd	nd
07/03/2012 am	Tarissan crater	127	5.2	0.005	0.013	24.4	95.3	3.9	0.8	0.004	0.009
07/03/2012 pm	Tarissan crater	85	4.1	0.003	nd	20.7	94.3	4.6	1.1	0.003	nd
05/03/2012 pm	Ty fault	16	24.5	0.001	0.011	0.7	38.7	58.8	2.4	0.002	0.027

nd: not detected.

Fig. 4. H₂S–H₂O–CO₂–SO₂–H₂ concentrations (ppmv) in SC volcanic plume measured with MultiGAS in March 2012. (a) Detail of La Soufrière summit lava dome (SC area) showing the tracks of typical orthogonal (A–D) and co-axial (X–Y) walking traverses in SC plume on March 7. Gas concentrations along (b) the orthogonal walking traverse A–D and (c) the co-axial traverse X–Y. Travelled distances (in metre) from start-point of the tracks (A and X) are shown on the x-axis.

concentrations of other gas species are reported in Table 1 as molar percentages of the 100%-normalized 'dry' gas phase. Low N₂ and O₂ amounts demonstrate minor air contamination, essentially from ambient atmosphere according to N₂/Ar ratios that are close to the air ratio (83). Carbon dioxide is the main gas species, followed by H₂S, H₂ and SO₂. CH₄ and CO are the minor components. Despite enhanced degassing, SC fumarolic fluid in March 2006 and March 2012 displays a broadly similar composition, with steady CO₂/H₂S and CO₂/HCl ratios and high H₂S/SO₂ ratio. Finally, helium is highly enriched with respect

to its potential contribution from contaminating air, in agreement with its MORB-type ³He/⁴He ratio (7.9 to 8.3 Ra; Table 1). Instead, the average CO₂/³He molar ratio of 10¹⁰ (corrected for air contamination) is about 5 times higher than the mean ratio in MORB mantle (2.2 ± 0.4 × 10⁹; Marty and Tolstikhin, 1998). Such a high ratio indicates an ultimate crustal derivation of about 80% of the emitted carbon dioxide, most likely from the subducted slab according to geochemical evidences of a subducted sediment contribution to magma genesis under the arc (Van Soest et al., 1998; Pedroni et al., 1999, and references therein). A

subducted sedimentary contribution is also compatible with the higher mean $\delta^{13}\text{C}$ ($-3.2 \pm 0.6\text{‰}$) of La Soufrière CO_2 compared to typical MORB upper mantle carbon (-8 to -5‰ ; Allard, 1983, 2006; Javoy et al., 1986; Ruzié et al., 2013).

4.2. March 2006 plume observations

Fig. 3a shows the time-averaged distributions of H_2S (ppmv), water vapour (g m^{-3}) and temperature ($^\circ\text{C}$) in the core (at half thickness) of La Soufrière (SC) volcanic plume in March 2006, as retrieved from our traverse orthogonal to the blowing plume direction only 5 m downwind SC fracture vent. The volcanic plume cross-section is well defined by the data. At the onset of our traverse, the lack of H_2S and the T- H_2O air values are representative of pure background atmosphere previously measured upwind of the vent. The sharp increase of H_2S and water vapour, together with temperature, after 5 m of the profile and their drop back to air values after about 40 m distance (Fig. 3a) delineate a maximum width of 35 m for the plume cross-section. Measurements of the vertical distribution of the three parameters at each point constrain an average plume thickness of 2 m: no H_2S and pure air background T and RH values were generally detected at ≤ 0.2 and ≥ 2.2 m height above the ground, except during occasional turbulent wind fluctuations. H_2S iso-contours drawn by applying geostatistical kriging (Surface Mapping System Surfer software, Version 8) to our horizontal and vertical data set verify that the core of the plume, characterized by maximum H_2S concentrations, stands at between 1 and 2 m height above ground level (Fig. 3b). Statistical processing just tends to overestimate H_2S concentration at maximum height where our number of data points is more limited. In the core portion of the plume, H_2S , H_2O and temperature display very parallel variations (Fig. 3a) and, in agreement with field observations, their average values evidence a more intense fumarolic supply from the northern section (SCN) than southern section (SCS) of SC fracture vent (Fig. 3a and b). H_2S varies between 24.7 and 42.0 ppmv, H_2O between 12.6 and 19.8 g m^{-3} (RH from 79.3% to 97.7%), and temperature between 17.8 (ambient) and 22.9 $^\circ\text{C}$. Comparing these plume features to the characteristics of the fumarolic fluid at exit (108.5 $^\circ\text{C}$, 97.8 mol% H_2O and 5900 ppmv H_2S ; Table 1) highlights how the latter becomes rapidly air-diluted and cooled upon emission, through turbulent expansion and mixing: the maximum H_2S plume content of 42 ppmv points to an air dilution factor of 140 only 5 m downwind of the vent under stable weather conditions. However, while being strongly air-diluted the volcanic plume remains 2–3 $^\circ\text{C}$ hotter than ambient atmosphere and thus produces a clear thermal anomaly in infrared imaging (see below and Beauducel et al., submitted for publication).

Fig. 3c shows the evolutions of H_2S , H_2O and temperature in the core of SC plume (~ 1.5 m height above the ground) along its blowing axis at distances of 2 to 55 m from SC northern vent (SCN, point 15 m on x-axis of Fig. 3a). Over that path length one observes a quite regular, exponential decrease of H_2S from 49 to 3.8 ppmv, which in first order fits with pure air dilution during plume dispersion from a linear gas source under the measured atmospheric conditions (Pasquill, 1961). Bernard et al. (2006) reported a similar H_2S trend in SC plume in September 2004, but with lower absolute concentrations (e.g., 8 ppmv compared to ~ 30 ppmv at 15 m distance from SC) which may reflect either a lower emission rate at that time or/and more efficient air-dilution of the plume due to much higher wind speed (12 m s^{-1}) during their measurement. In the very first part of our profile (2–10 m from the vent) the decrease of H_2S is paralleled by a rapid decrease of both temperature (from 22 to 18.5 $^\circ\text{C}$) and water vapour (Fig. 3c). Afterwards, the plume gradually reaches the contemporaneous air background temperature (16 $^\circ\text{C}$ by the end of the day), while its vapour content remains at a high level (14–12 g m^{-3} , i.e. RH ~ 95 –90%). Such a pattern is well explained by entrainment of air moisture during plume dilution. Fig. 3d shows the modelled 2-D horizontal evolution of H_2S iso-contours during SC plume dispersion and dilution obtained by geostatistical kriging

of our results for both the orthogonal traverse and the axial profile at the plume's core height.

4.3. March 2012 MultiGAS observations

MultiGAS measurements in March 2012 allowed us to determine the H_2O – CO_2 – H_2S – SO_2 – H_2 composition of gases issuing from each of the active vents (Table 2) and then to determine the total plume fluxes from both SC and TAS craters. Below we focus on results for SC vent, the most active one. Fig. 4a–b shows a typical traverse orthogonal to the transport direction of SC plume, obtained on March 7. In the upwind side of the profile (from A to B) and outside the plume's margins, SO_2 and H_2S are at or below the detection limit (<0.1 ppm) and the relatively stable concentrations of H_2O ($\sim 17,000$ ppmv), CO_2 (~ 385 ppmv) and H_2 (~ 0.7 ppmv) are representative for air background on top of the volcano. As the plume is intercepted (B) the concentration of all gas species consistently increases, reaches its maximum at the plume axis (C in Fig. 4b), then returns to nearly-background values at the end of the plume's encounter (D). Note that H_2S displays a much higher plume/background contrast (~ 700) than CO_2 (~ 3.3) and H_2O (~ 1.3) at the plume axis. In the plume cross section B–D (~ 60 m wide) all gases but H_2O exhibit rapid oscillations, illustrating the fast response of the sensors to variable plume density (pulsations in plume speed and direction). The far less nervous behaviour of H_2O is consistent with both its higher content in the volcanic fluid and the high relative humidity (as high as 94%) of ambient air. Because the plume was so close to vapour saturation and partial condensation, we cannot exclude some vapour loss (as condensed water) in the instrument's pipeline. This means that our measurements may underestimate to some (likely minor) extent the real H_2O emission. All the orthogonal traverses performed at SC during March 5–7 yielded similar output as that shown in Fig. 4b (a cumulative H_2S concentration profile obtained by summing the results of all the traverses is shown in Fig. 5d).

Fig. 4c shows the results of a typical axial profile performed on March 7 along the blowing direction and in the core of SC plume. Over the explored distance range (~ 5 m from vent at X to ~ 70 m at Y; Fig. 4a,c) the concentration of all measured gases decreases with increasing distance, even though with an irregular pattern in the first 20 m. As the profile end is approached, all gas concentrations have fallen to low levels (e.g., $\text{H}_2\text{S} \sim 2$ ppm, $\text{SO}_2 \sim 0.1$ ppm) but still above the air background. Such a spatial trend is consistent with increasing air dilution of the volcanic plume. However, Fig. 4c also shows that while $\text{SO}_2/\text{H}_2\text{S}$ and $\text{CO}_2/\text{H}_2\text{S}$ ratios remain low and stable until about 20 m from the vent, they monotonically increase at higher distance, with a sharper rate after 45 m. This pattern points to H_2S depletion relative to CO_2 and SO_2 after short plume transport time, evidencing that H_2S oxidation in tropical wet volcanic plumes is much faster than observed in colder and less humid environments (e.g., Italy; Aiuppa et al., 2005b, 2007). This observation implies that our H_2S -based flux assessment in March 2006 is reliable for only near-vent (<20 m) plume measurements (see thereafter).

In order to explore the variability of gas concentrations along vertical cross-section(s) of the plume, we performed a number of vertical MultiGAS profiles by sequentially moving the instrument's inlet from the ground level up to ~ 3.5 m height. Fig. 5e gives an illustration of the variations in H_2S concentration measured at a fixed position in the core of the SC plume (site C in Fig. 4a,b). One sees that the bulk of the plume was captured between ~ 0.5 and ~ 3 m height above the ground, with maximum H_2S concentrations of ~ 50 ppm. The spread of concentrations recorded at any given height reflects the temporal variations in plume density resulting from instantaneous random changes in wind strength and direction. Low H_2S concentrations (down to background level) at heights of <0.5 m and ≤ 3.5 m above the ground (Fig. 5d) verify that the volcanic plume was essentially confined at close-to-ground level during our MultiGAS measurements (average

Fig. 5. Horizontal and vertical concentration profiles of H₂S in SC and TAS volcanic plumes in March 2012. Maps show (a) the summit lava dome and (b) the area of SC and TAS craters and their plumes. Variations in H₂S concentration along X (horizontal distance) and Y (height above ground) in the ellipsoidal cross section of both plumes are depicted by the colour scale from blue (low values) to dark red (high values). These were calculated from the horizontal and vertical profiles shown in (c, d) and (e), and by combining Eqs. (1) and (2) (see text). (c) Horizontal H₂S concentration profile across TAS volcanic plume (1.2 m height above the ground); (d) cumulative horizontal H₂S concentration profile, obtained by summing the results of all MultiGAS traverses orthogonal to the SC plume; and (e) vertical profile (Y, in m) of H₂S concentrations (Z, in ppm) obtained in the core of SC plume (e.g., at horizontal distance X = 43 m from A, along the track A–D of Fig. 4).

thickness ≤ 2.5 m) and, therefore, that we were able to capture most of the volcanic gas discharge.

4.4. IR-camera observations

The IR camera was positioned at 80 m NNW from the plume arising from the SC fracture, in order to get a complete lateral plume viewing. Fig. 6a shows a representative example of the velocity vectors calculated

from each couple of images and the particle image velocimetry (PIV) algorithm (Mori and Chang, 2003). We observe a vertical gradient in horizontal speed from 5 m/s at ground level to 15 m/s at the top of the plume, with a mean value of 7.6 m s^{-1} at height of the plume's core. Comparable wind speeds ($7\text{--}14 \text{ m s}^{-1}$) were measured at the same time and at heights of 1.5–2.5 m in the plume using a hand-held anemometer. Our image analysis of other 2 s IR camera movies provided us with similar ranges and average velocities as in Fig. 6a. We

Fig. 6. Measurements of SC plume's thickness and velocity from thermal infrared 2-s length movie (March 2012). (a) Representative sample of image with velocity vectors and (b) stack of the 50 images. Graphs on the right: (y-axis) mean values of velocity for each elevation layer, (x-axis) histogram of velocities.

therefore use a mean plume velocity of 7 m s^{-1} in all calculations below (cfr. 5.2).

To determine the plume thickness, we calculated a stack of 50 images, corrected for camera shaking using vectors on the ground part of each image. The results displayed in Fig. 6b constrain an average plume height of 3.5 m, in fair agreement with the highest plume thickness inferred from MultiGAS measurements (Fig. 5e).

5. Discussion

5.1. Vent-to-vent gas comparison

Our MultiGAS data for the different active vents of La Soufrière lava dome in March 2012 allow the very first comparison of their gas emissions at a same time. Data for each vent were combined to draw gas/ H_2S correlation plots, since H_2S is the best volcanic marker (with highest plume/background contrast; Section 4.3). Fig. 7 illustrates the coherent distributions between H_2S and the four other gas species in SC plume, based on the dataset presented in Fig. 4. The gradient of the best-fit regression line in the concentration plots provides the average gas/ H_2S molar ratios of the emitted volcanic gas (e.g. Aiuppa et al., 2011). Table 2 lists the average chemical ratios and hence the molar gas composition obtained for each vent.

Our results demonstrate a substantial vent-to-vent variability of La Soufrière gas emissions. Plume emissions from SC vent confirm the release of a water-dominated volcanic gas (~96–97%), with 2.0–2.9% CO_2 and ~1% H_2S (Table 2). When compared to the hot fumarolic fluid sampled simultaneously (Table 1), SC plume displays similar $\text{CO}_2/\text{H}_2\text{S}$

(2.2–2.7 vs 2.3) and $\text{H}_2/\text{H}_2\text{S}$ (0.013–0.018 vs 0.0145) ratios, which verifies a good conservation of H_2S at short transport range. Its higher $\text{SO}_2/\text{H}_2\text{S}$ ratio (0.025–0.04) than in the hot fluid (0.010–0.013) thus suggests some partial loss (dissolution, precipitation) of poorly abundant SO_2 in collected samples of the hot fluid prior to their analysis. The Gouffre 1956 (GF56) is found to emit the same gas as SC (Table 2), despite its far lower emissivity. In contrast, the exhalations from TAS and LC have much higher $\text{CO}_2/\text{H}_2\text{S}$ ratios (4.1–5.2 and 2.8–6.5, respectively) and $\text{H}_2\text{O}/\text{H}_2\text{S}$ ratios (85–263 and 168–260, respectively).

These compositional differences amongst the vents are clearly depicted in a scatter diagram of $\text{H}_2\text{O}/\text{CO}_2$ versus $\text{H}_2\text{O}/\text{S}$ (Fig. 8), in which La Soufrière data are also compared with other volcanic gas compositions in the Lesser Antilles arc. Two interesting observations arise from this diagram:

- Each Soufrière vent defines a characteristic, nearly linear data trend along which the gas composition varies from water-rich ($\text{H}_2\text{O}/\text{CO}_2 > 40$) to water-poorer ($\text{H}_2\text{O}/\text{CO}_2 < 20$) at almost constant CO_2/S (or $\text{CO}_2/\text{H}_2\text{S}$) molar ratio. Such linear patterns indicate that most of the compositional variability at individual vent is governed by variable extent of water-loss from or water-addition to an otherwise steady gas phase (constant C/S ratio). Water loss can arise from steam condensation (in the ground, or prior to sensing by the MultiGAS) and water gain can result from variable incorporation of external meteoric water into either the feeding conduits or the plume.
- Instead, the differences in CO_2/S ratio amongst the vents are best explained by variable extent of sulfur loss from an originally common volcanic gas (Fig. 8). For instance, S-poor gases from TAS can be

Fig. 7. Gas–H₂S scatter plots for SC plume from MultiGAS dataset of Fig. 4b. Gas/H₂S average ratios (Table 2) were obtained from the gradient of the best-fit regression lines.

interpreted as resulting from 45% mean S removal from a SC-type gas. The TAS crater actually hosts an acidic boiling lake ($T \sim 98^\circ\text{C}$, $\text{pH} = -0.46$ in March 2012) at ~ 85 m depth below its rim; sulfur scrubbing during gas–lake interaction can thus easily explain both the higher $\text{CO}_2/\text{H}_2\text{S}$ ratio and the marked SO_2 -depletion of its plume emissions (Table 2), as well as their high variability in H_2O . Hydrothermal degassing along the Ty fault at the base of the lava dome, characterized by a cluster of steaming vents with low flow rate ($T = 30$ to 95°C) and warm grounds, display the largest $\text{CO}_2/\text{H}_2\text{S}$ (24.5) and lowest $\text{H}_2\text{O}/\text{CO}_2$ (0.7) ratios (Fig. 8), consistent with extensive steam condensation and solid sulfur deposition in the local volcanic ground.

Our observations thus reveal significant compositional differences amongst La Soufrière vents, due to secondary and likely shallow alterations. The most pristine volcanic fluid is emitted from the most active SC vent. A limited influence of sulfur scrubbing at this vent in March 2012 is supported by the fact that SC fumarolic emission has a comparable CO_2/S ratio as high-temperature (740°C) magmatic gas directly collected in 1996 from the extruding andesitic lava dome of Soufrière Hills

in Montserrat (Hammouya et al., 1998), three weeks before the first pyroclastic flows. Note also that in 1997, prior to intensification of the current degassing unrest, SC fumaroles were a factor ~ 5 poorer in sulfur ($\text{CO}_2/\text{H}_2\text{S} \sim 10$) than in March 2006 and 2012 (Fig. 8). Clearly, this increased S content claims for either (i) highly reduced sulfur scrubbing compared to 1997, (ii) enhanced S remobilisation from the hydrothermal system, or/and (iii) increased sulfur supply from the degassing magma reservoir at depth, as discussed in Section 5.4.

5.2. Fumarolic gas fluxes

The volcanic gas flux in March 2006 was computed by integrating the horizontal and vertical distributions of H_2S in SC plume cross-section (Fig. 3b) and then multiplying by the wind speed. From the integrated amount of H_2S in the plume cross-section ($2610 \text{ ppm} \cdot \text{m}^2$), an average wind speed of $3.6 \pm 0.2 \text{ m s}^{-1}$ and the molecular weight of H_2S (0.034 kg), we obtain an H_2S output of $0.0127 \pm 0.007 \text{ kg s}^{-1}$ or $1.1 \pm 0.2 \text{ tons per day (t/d)}$ (Table 3). Scaling the composition of SC hot fumarolic fluid (Table 1) to this H_2S flux of $\sim 1 \text{ t/d}$, we then compute daily mean fluxes of 75 tons of H_2O , 2.8 tons of CO_2 , 0.45 tons of HCl , 0.04 tons of SO_2 and 0.0014 tons of H_2 (Table 3). We estimate an overall uncertainty of $\pm 30\%$ on these fluxes from the propagation of analytical errors. Water vapour contributes 94% of the total fluid output (80 t/d).

Our much larger dataset and for five gas species measured with MultiGAS in March 2012 allows improved flux quantification. We limit here our analysis to SC and TAS, by far the two main degassing vents; degassing at GF56 and LC vents was too weak for allowing any reliable in-plume traverse and, according to visual observations, contributes negligibly to the overall gas output. To calculate the volcanic gas flux we focus again on H_2S , the best volcanic marker. We computed the integrated amount (IA) of H_2S over the plume cross-section and multiplied by the mean plume transport speed given by thermal IR imagery. We restrict our flux assessment to March 7 during which both types of measurement were conducted simultaneously.

The procedure to derive IAs is illustrated in Fig. 5 for SC plume emission. We first used the cumulative H_2S concentration profile shown in Fig. 5d. As previously observed in March 2006 (Section 4.2), this profile shows two distinct gas contributions from the northern and southern sections of SC venting fracture and is best fitted by a double Gaussian function:

$$[\text{H}_2\text{S}]_x = a_1 e^{-\left(\frac{x-b_1}{c_1}\right)^2} + a_2 e^{-\left(\frac{x-b_2}{c_2}\right)^2} \quad (1)$$

where $[\text{H}_2\text{S}]$ is the concentration (in ppm), x is the horizontal length in plume's cross section (in m), and a_1 , b_1 , c_1 , a_2 , b_2 , and c_2 are the fit-constants for Gaussians 1 and 2 that take respective values of 32.6, 43.1, 9.8, 20.4, 34.8 and 33.5. We then used the results of vertical profiles (e.g. Fig. 5e) to derive the Y dependence of H_2S plume concentrations. The latter is best fitted with the following polynomial function:

$$[\text{H}_2\text{S}]_y = -0.78y^5 + 0.05y^4 + 27.3y^3 - 96y^2 + 119y - 0.91 \quad (2)$$

where y is the height above ground (in m). Functions (1) and (2) were then combined to obtain numerical values of a $[\text{H}_2\text{S}]_{x,y}$ concentration function over the entire cross-section of the plume, which is taken as ellipsoidal (Fig. 5b). Integration of this function yields a total H_2S amount of $3940 \text{ ppm} \cdot \text{m}^2$, or 0.005 kg m^{-1} (Table 3). Multiplied by a plume transport mean speed of 7 m s^{-1} (range: 5 – 15 m s^{-1}), this amount converts into an average H_2S flux of $0.035 \pm 0.010 \text{ kg s}^{-1}$ or $3.0 \pm 0.8 \text{ t/d}$. This is about three times higher than our H_2S flux estimate of $\sim 1 \text{ t/d}$ in March 2006. Such a difference goes beyond the uncertainties introduced by the use of different analytical tools in 2006 and 2012 and thus suggests a slight (but detectable) sulfur flux increase at SC vent in the 6-year interval, coherent with the observed increase of degassing activity. Using the average bulk composition of SC plume (Table 2), we

Fig. 8. H_2O/CO_2 vs H_2O/S molar ratios in plume exhalations from the different active vents of La Soufrière in March 2012 (Table 2), compared with published data for other volcanic-hydrothermal gas emissions in the Lesser Antilles arc. Data sources: [1] This work; [2] Bernard et al., 2006; [3] Brombach et al., 2000; [4] Hammouya et al., 1998; [5] Chiodini et al., 1996; [6] Di Napoli et al., 2013; [7] Allard, 1981; [8] D'Amore et al., 1990.

then compute a total gas flux of ~ 160 t/d ($\pm 25\%$), with H_2O (~ 150 t/d) and CO_2 (9 t/d) as main contributors (Table 3). This corresponds to a total volumetric output of about $5 \text{ m}^3 \text{ s}^{-1}$ of purely volcanic fluid at ambient pressure. Since SC volcanic plume entrains and heats abundant ambient humid air (Section 5.1), we emphasize that volumetric flux assessment based on simple thermal imagery of the bulk plume could overestimate the actual flux of volcanic steam, whereas the latter is determined specifically by direct MultiGAS analysis.

By applying the same procedure to our dataset for the volcanic plume from TAS crater (Fig. 5) we obtain an H_2S flux of 1.0 ± 0.2 t/d and a bulk fluid flux of 60 ± 15 t/d (Table 3) from this vent. While being ~ 2.5 times less productive than SC, TAS emitted in 2012 about as much gas as SC in 2006 (Table 3), which illustrates the strength of renewed activity at that crater in recent years. Moreover, taking account of $\sim 45\%$ sulfur scrubbing in TAS crater lake (Section 5.1 and Fig. 8), the sulfur gas supply to this crater may actually be ~ 1.5 t/d. We have no data for the chlorine flux from TAS, which leads to somewhat underestimate the total Cl fumarolic output from the volcano. Nevertheless,

because water vapour highly predominates in the fumarolic fluid, the total (SC + TAS) fumarolic fluid flux from La Soufrière in March 2012 is correctly evaluated as about 220 t/d. This is much less than the steam flux of 10^3 – 10^4 t/d estimated during the 1976–1977 phreatic eruptions or even than the average daily steam flux during that eruptive period (Le Guern et al., 1980). In its present stage of activity La Soufrière thus remains a weak gas emitter. However, it is the second most important spot of volcanic degassing in the Lesser Antilles arc, after Soufriere Hills of Montserrat where lava dome extrusion since 1996 has been accompanied by a time-averaged SO_2 flux of ~ 600 t/day and pulses at >5000 t/day (Christopher et al., 2010). La Soufrière emissions are of the same order as those measured at other closed-conduit quiescent volcanoes in degassing unrest. One example of these is Vulcano island (Italy), where characteristic H_2O and H_2S fluxes are comparable (225–580 t/d and 7.5–8 t/d; Tamburello et al., 2011). But Vulcano also produces 20–27 t/d of SO_2 (Tamburello et al., 2011), whereas La Soufrière emits very few SO_2 (~ 0.2 t/d; Table 3) and hence displays a more typical hydrothermal signature.

Table 3

Steam and gas fluxes from La Soufrière summit fumarolic activity. Comparison with chemical fluxes through thermal water outflow.

	South crater 03/2006	South crater 03/2012	Tarissan 03/2012	Total flux 03/2012	Hot springs Discharge ^b	Gas/spring Flux ratio
Plume speed (m/s)	3.6	7.0	7.0			
H_2S IA ^a (ppm·m ²)	2610	3940	1360			
H_2S flux (tons/day)	1.0	2.8	1.0	3.8	0.17	22
H_2O flux (tons/day)	75	149	54	203	830	0.24
CO_2 flux (tons/day)	2.8	9.0	5.8	14.9	0.026	572
HCl flux (tons/day)	0.45	1.1	–	1.1	0.17	6.5
SO_2 flux (tons/day)	0.04	0.19	0.01	0.2		
H_2 flux (tons/day)	0.0014	0.003	0.17	0.17		
Total (tons/day)	79	163	61	224	830	0.3
^3He (mole/day)	$5.8E-06$	$2.1E-05$	$1.3E-05$	$3.4E-05$	$1.3E-08^c$	2600

See the text for details and discussion.

^a Integrated amount of H_2S in volcanic plume cross-section (see Section 5.1).

^b Total chemical fluxes through thermal water outflow, as detailed in Table 4, with dissolved S expressed as H_2S for direct comparison with fumarolic emission.

^c From Ruzié et al. (2012).

5.3. Total volatile output and thermal budget of La Soufrière

In addition to fumarolic summit degassing, hydrothermal manifestations at La Soufrière include thermal springs and diffuse soil gas emanations whose contribution to the chemical and heat budget of the volcano must also be considered.

Six hot springs issue at high elevation (1145–980 m a.s.l.) around the lava dome, within 1.4 km from its top, from within the former crater in which the dome has built (see their location in Villemant et al., 2005). Their chemistry and flow rate are routinely monitored by the volcano Observatory (OVSG-IPGP reports, 1992–2012). These springs contain dissolved helium and CO₂ with fumarole-like magmatic isotopic signatures (~8 Ra and −5.4 to −3.2‰, respectively; Allard, 2006; Ruzié et al., 2012, 2013; Jean-Baptiste et al., 2013), as well as magma-derived chlorine (Li et al., 2012). Table 4 lists the spring characteristics relevant to our study. From their average flow rate and chemistry in March 2006 and March 2012, we compute a total hot water outflow of 830 tons d^{−1} carrying about 0.026 t/d of carbon (as CO₂), 0.16 t/d of S and 0.16 t/d of Cl (Table 4). This budget is conservative since some springs (e.g. Ravine Marchand) issue from a wider area than surveyed. It reveals that the thermal water discharge from La Soufrière is four times larger by mass than the fumarolic steam output but contributes comparatively little CO₂ (0.17%) and a small proportion of S (4.5%) (Table 3). Its higher relative contribution in chlorine (~20%) is consistent with the higher solubility of HCl than CO₂ and S-bearing gas species in groundwater. This comparison demonstrates a gaseous transfer and release of virtually all (>99%) carbon dioxide and of most (>95%) of total sulfur through the central conduits of the volcanic pile. A prominent central gas transfer is especially obvious for ³He, little soluble in groundwater, whose flux from summit fumaroles is three orders of magnitude higher than its thermal spring discharge (Ruzié et al., 2012; Table 3).

Diffuse soil degassing is a third mode of volatile release at La Soufrière. Diffuse soil emanations of CO₂-rich gas were initially identified at the base of the lava dome, in the hydrothermal zone extending along the regional Ty fault (Allard et al., 1998; Fig. 1d). Here as well, the emanating CO₂ and He have a magmatic isotopic signature similar to that in summit fumaroles (Allard, 2006; Ruzié et al., 2012; Jean-Baptiste et al., 2013). In March 2006 we performed the very first measurements of soil CO₂ fluxes at La Soufrière. Tropical vegetation covering the summit area produces a background biogenic CO₂ flux of 0.06 to 0.16 kg m^{−2} d^{−1}. On the lava dome, made of massive lava (Nicollin et al., 2006), we could not find any gas flux anomaly with respect to this biogenic background, except at a few points of steaming ground surrounding SC vent (Fig. 9a). The only area of intense volcanic soil degassing was again verified along the Ty fault at the base of the dome. In addition to high temperatures (60 to 93 °C) and high

CO₂ concentrations (from 10 to 100 mol%) at 30–70 cm depth in the ground, the fault structure is characterized by relatively high CO₂ flux values (up to 20 kg m^{−2} d^{−1}) but within only two narrow sections of our profile (Fig. 9b). By integrating the CO₂ flux in these two emissive bands and extrapolating to their respective area (~15 × 3 m and 10 × 2 m), we crudely estimate a total soil CO₂ flux of 0.3 t/d, equivalent to 10% of the fumarolic CO₂ flux in March 2006 and only 2% of the fumarolic flux in March 2012 (Table 3). Our MultiGAS data for the H₂O/CO₂ (0.7) and CO₂/H₂S (24.5) ratios of gas emanations along the Ty fault (Table 2) lead to corresponding fluxes of 0.2 t/d of steam and 0.02 t/d of H₂S. Therefore, in the present stage of activity soil degassing contributes only a minor part to the bulk CO₂ and S emissions from La Soufrière and negligibly to its steam (and heat) output, in agreement with estimates from airborne thermal imaging (Beauducel et al., submitted for publication).

The thermal budget of La Soufrière can thus be quantified from the fluid fluxes associated with both summit fumarolic degassing and thermal spring outflow. As shown above, water vapour constitutes ~97–98 mol% of the fumarolic emission (Tables 1 and 2) and 94% of its bulk mass output (Table 3). Therefore, the enthalpy of fumarolic activity (Q_{tot} , kJ s^{−1}) is essentially due to heat release by cooling and condensation of the volcanic steam flux (M_v , kg s^{−1}):

$$Q_{\text{tot}} = M_v \cdot [C_{p,v} \cdot (T_v - T_b) + L_c + C_{p,l} \cdot (T_b - T_a)] \quad (3)$$

where $C_{p,v}$ is the specific heat (2.0156 kJ kg^{−1} °K^{−1} at ~0.9 bar) released during cooling of the superheated steam from its exit temperature T_v (108.6 in 2006, 107.5 °C in 2012) to the water boiling temperature (T_b = 96.7 °C) at the dome altitude, L_c is the latent heat of condensation (2265.55 kJ kg^{−1} at 0.9 bar), and $C_{p,l}$ is the heat capacity (~4.2 kJ kg^{−1} °K^{−1}) of liquid water cooled from T_b to the ambient air temperature T_a . In computing the thermal budget in March 2012 we consider the emissions of superheated steam from SC and of boiling steam (~98 °C) from TAS acid lake. The fumarolic steam flux of ~0.9 kg s^{−1} in March 2006 and 2.6 kg s^{−1} in March 2012 results in respective heat release of 2.3×10^3 and 6.9×10^3 kJ s^{−1}, or 2.3 and 6.9 MW.

From the measured temperature and flow rate of the hot springs (Table 4), we compute a cumulated heat release of 1.1 MW as the waters cool to air temperature at their exit. Although prevalent by mass, the thermal water outflow thus contributes the equivalent of only 17% of the fumarolic heat release. We therefore assess a total enthalpy budget of about 8 MW from La Soufrière in March 2012. This is about half the power production of the Bouillante geothermal plant (15 MW; Sanjuan and Brach, 1997), 18 km away on the western coast

Table 4
Mean water outflow and CO₂–S–Cl budget of La Soufrière thermal springs in March 2006 and March 2012.

Spring	Altitude m a.s.l.	Date	T °C	pH	Cond. mS	Flow rate l/min	HCO ₃ mg/l	SO ₄ mg/l	Cl mg/l	CO ₂ tot. kg/day	S kg/day	Cl kg/day
Carbet l'Echelle	1146	24/03/2006	21.2	5.19	936	4.5	55.5	864.6	21.3	0.26	1.9	0.1
Carbet l'Echelle		28/03/2012	20.8	5.28	1275	3.2	62.0	727.0	11.2	0.20	1.1	0.1
Galion	1100	22/03/2006	44.2	4.93	1890	160	36.0	720.5	244.6	5.98	55.3	56.4
Galion		13/03/2012	47.9	5.25	3050	150	35.1	679.9	457.7	5.47	48.9	98.9
Galion bis	1100	10/01/2006	41.9	5.05	1794	120	25.3	569.8	193.1	3.15	32.8	33.4
Galion bis		13/03/2012	42.8	5.38	2380	110	30.9	589.9	378.7	3.53	31.1	60.0
Tarade	1079	28/03/2006	37.2	5.86	1533	139	94.0	707.3	139.1	13.6	47.3	27.9
Tarade		09/03/2012	41.5	5.97	2188	79	107.5	681.3	183.1	8.84	25.9	20.9
Ravine Marchand	1015	22/03/2006	43.5	5.30	1220	19.0	78.1	489.9	39	1.54	4.5	1.1
Ravine Marchand		13/03/2012	44.7	5.55	2094	24.2	94.8	490.6	112.8	2.38	5.7	3.9
Pas du Roy	1008	28/03/2006	33.5	5.56	940	13.3	54.3	460.1	54.7	0.75	2.9	1.0
Pas du Roy		09/03/2012	34.6	5.59	1213	24.6	40.9	431.2	64.8	1.05	5.1	2.3
Bains Jaunes	981	28/03/2006	30.4	5.28	723	159	16.5	355.4	49.6	2.72	27.1	11.4
Bains Jaunes		01/03/2012	29.6	5.35	850	144	16.8	285.6	50.2	2.52	22.4	12.0
Total flux (kg/day)						830 × 10 ³				26	156	165

Chemical analyses were performed at La Soufrière volcano Observatory (OVSG) using routine procedures (acid titration and ion chromatography). Water physical parameters measured on the spot (conductivity normalized at 20 °C). The location of hot springs is given on the OVSG-IPGP web site (<http://volcano.ipgp.fr/guadeloupe/Infos.htm>) and in Villemant et al. (2005).

Fig. 9. CO₂ flux from volcanic soil degassing at La Soufrière in March 2006. (a) Profiles on and around the lava dome (blue: no anomaly with respect to the background biogenic flux; red: volcanic flux anomalies). (b) Details of soil gas profiling across the Ty fault at the base of the dome. CO₂ concentrations ($\pm 3\%$) and temperature (± 0.1 °C) were measured at 30–70 cm depth in the ground, using a portable infrared spectrometer (ADC LFG-20) and a thermocouple, respectively. Volcanic CO₂ fluxes ($\pm 5\%$), corrected for ambient pressure, were measured at the soil interface with a portable Dräger infrared spectrometer coupled to a West System accumulation chamber (Chiodini et al., 1998). High ground CO₂ concentrations (10–100%) and temperature (up to 95 °C), as well as high CO₂ flux values (up to $20 \text{ kg m}^{-2} \text{ d}^{-1}$), characterise two narrow bands coinciding with the Ty fault.

of Basse Terre island. Comparing with the contemporaneous seismic energy release is also interesting: over the past ten years the latter averaged 15 MJ yr^{-1} (OVSG-IPGP reports) which, in terms of instantaneous mechanical energy release, corresponds to a trivial rate of 0.5 W. Therefore, in the present stage of activity the energy budget of La Soufrière is overwhelmingly due to hydrothermal manifestations.

5.4. Magma degassing supply

As introduced, La Soufrière hydrothermal activity is sustained by heat and gas transfer from a long-lived ($>30 \text{ ka}$; Touboul et al., 2007) andesitic magma reservoir, repeatedly replenished with basalt from below, whose roof stands at about 6–7 km depth beneath the summit

(Hirn and Michel, 1979; Pozzi et al., 1979; Feuillard et al., 1983; Poussineau, 2005; Boudon et al., 2008). Petrologic experiments on the 1530 AD eruptive products (Poussineau, 2005) constrain that the reservoir is confined under mean P–T–redox conditions of 160 MPa (~6.5 km depth), ~875 °C and $\log f_{\text{O}_2} \sim \text{NNO} + 0.8$ (where NNO is the nickel–nickel oxide redox buffer). Continuous gas transfer from this reservoir is evidenced by the magmatic isotopic signatures of He, CO₂ and Cl in La Soufrière hydrothermal fluids in the past 35 years (Allard et al., 1982; Allard, 1983, 2006; Van Soest et al., 1998; Pedroni et al., 1999; Li et al., 2012; Ruzié et al., 2012, 2013; Jean-Baptiste et al., 2013). In contrast, D/H and ¹⁸O/¹⁶O data point to a prominent meteoric derivation of the fumarolic steam through the boiling of local groundwater (Benauges, 1981; Brombach et al., 2000; Allard, 2006 and in preparation). The origin of sulfur may be more complex: its isotopic composition is not known and this element is more susceptible to fractionation during gas–water–rock interactions (Symonds et al., 1994). However, we have shown above that only a small fraction (<5%) of total emitted sulfur is actually scrubbed in La Soufrière thermal aquifers (Section 5.3 and Table 3) and, secondly, that fumarolic degassing from SC vent, the least affected by scrubbing (Section 5.1) and responsible for most of the gas output (Section 5.2), has a comparable CO₂/S ratio as degassing from early andesite extrusion at Soufrière Hills of Montserrat (Fig. 8). Therefore, a co-magmatic derivation of CO₂ and S in SC fumarolic gas and, more broadly, in the deep gas supply to La Soufrière hydrothermal system is a reasonable hypothesis. The predominant release of sulfur as H₂S (Table 1) is not only coherent with the hydrothermal temperature of the fumarolic emission but also compatible with thermodynamic computation for magmatic gas on top of the andesitic reservoir: thermodynamic data (Barin and Knacke, 1973) for the equilibrium reaction $\text{H}_2\text{S} + 3/2 \text{O}_2 = \text{SO}_2 + \text{H}_2\text{O}$ under the P–T–redox reservoir conditions (Poussineau, 2005) constrain a high H₂S/SO₂ molar ratio (≥ 10) in the likely water-rich (see below) magmatic gas phase. Now, upon escape from the reservoir and ascent through the crust, this gas phase should become increasingly enriched in H₂S over SO₂ as it cools and re-equilibrates and, subsequently, as it interacts with the shallow hydrothermal system (scrubbing of more soluble SO₂ as sulfate).

Based on the above considerations, we can use the volcanic gas fluxes measured in March 2012 and available data for dissolved volatiles in La Soufrière magma in order to tentatively assess the quantity of underground magma from which free gas release supplies the current activity.

Petrologic and geochemical (major and trace elements) data for the erupted products of La Soufrière–Grande Découverte volcanic complex show that they belong to the same differentiation trend as older magmatic series from the Basse Terre Axial Chain and the southernmost Mount Caraïbes (Semet et al., 1981; Boudon et al., 2008) and that

their compositional range (from evolved basalt to felsic andesite and rarer dacite) is well explained by fractional crystallization from a parental basalt that replenishes the reservoir from below (Semet et al., 1981; Poussineau, 2005; Touboul et al., 2007; Boudon et al., 2008). Owing to its incompatible behaviour, K₂O and its content in the evolved magmatic liquids (represented by melt inclusions and glassy matrixes) are reliable indicators of the extent of this differentiation process (Boudon et al., 2008). Volatile abundances in the parental basalt of La Soufrière–Grande Découverte magmas are unknown but an indirect estimate is given by the volatile content of basaltic melt inclusions (48.2% SiO₂, 5.0% MgO and 0.6% K₂O) entrapped in olivines of the least evolved basalts from the nearby Mount Caraïbes massif: these were found to contain about 2 wt.% H₂O, 0.12 wt.% S and 0.14 wt.% Cl (N. Métrich, unpub. data, pers. comm. 2012; Table 5). In comparison, melt inclusions entrapped in pyroxene and plagioclase phenocrysts of La Soufrière andesites contain 4–5 wt.% H₂O, 0.25–0.30 wt.% Cl, 0.025 wt.% S and very few (≤ 25 wt. ppm) CO₂ (Semet et al., 1981; Poussineau, 2005; Boudon et al., 2008). These latter inclusions are all rhyolitic in composition (75% SiO₂ and 2.1% K₂O on average) and represent the most differentiated liquid of crystal-rich (40 wt.%) felsic andesite stored in the upper part of the magma reservoir (Semet et al., 1981; Poussineau, 2005; Boudon et al., 2008). Their dissolved volatile content well agrees with the respective solubilities of H₂O–CO₂ (Papale et al., 2006), S (Clemente et al., 2004) and Cl (Shinohara, 2009) in rhyolite under the P–T–redox confining conditions of the reservoir (Poussineau, 2005). Amphibole and sulfide globules are absent in La Soufrière evolved products (Poussineau, 2005; Boudon et al., 2008).

Hence, according to the above evidences the magma feeding system of La Soufrière is open to basaltic replenishment at its bottom and to gas escape from its top, supplying hydrothermal emissions at the surface. Since we have no information on the geometry and the degassing mode of this feeding system, here we just attempt to estimate the amount of feeding (basaltic) magma whose degassing would be needed to supply the 2012 volcanic fluxes of magma-derived volatiles. For doing this, we calculate the bulk mass fraction of H₂O, S and Cl exsolved in the magmatic system from the difference between the K₂O-normalized initial concentration of each species in the parental basalt and its K₂O-normalized residual concentration in the rhyolitic melt of andesite on top of the reservoir. Normalizing to K₂O allows to correct for magma differentiation. The exsolved mass fraction of each volatile is equal to: $1 - [(X_i/\text{K}_2\text{O})_r / (X_i/\text{K}_2\text{O})_b]$, where X_i is its respective concentration (wt.%) in the rhyolitic (r) and basaltic (b) melts. The results, listed in Table 5, indicate a bulk exsolution rate of 36% for water, 94% for sulfur and 45% for chlorine, corresponding to bulk exsolved amounts of 0.71 wt.% H₂O, 0.10 wt.% S and 0.063 wt.% Cl in the overall magmatic system. If one accepts a magmatic derivation of the total flux of

Table 5

Bulk exsolution rate and bulk exsolved amounts of H₂O, S, Cl and CO₂ in La Soufrière magma feeding system, as computed from the K₂O-normalized volatile concentrations (melt inclusions) in the deep feeding basalt and in the rhyolitic melt of felsic andesite stored at 6–7 km depth beneath the volcano. Compared compositions of the computed magmatic gas phase and of SC fumarolic fluid emitted in March 2012.

Species	Basalt ^a	Rhyolite ^b	$X_i/\text{K}_2\text{O}$	$X_i/\text{K}_2\text{O}$	Exsolution	Bulk exsolved	Magmatic	2012 SC
	Wt.%	Wt.%	Basalt	Rhyolite	Rate ^c	Amount (wt.%)	Gas (mol%)	Fluid (mol%)
H ₂ O	~2	4.5	3.33	2.14	0.36	0.714	74	96.7
S	0.11	0.025	0.18	0.012	0.94	0.103	6.0	0.9
Cl	0.14	0.27	0.23	0.13	0.45	0.063	3.3	0.4
CO ₂	0.4 ^d	0.0025	0.7	0.0012	0.998	0.399	17	2.0
K ₂ O	0.6	2.1						

^a Dissolved H₂O, S and Cl contents of basaltic melt inclusions entrapped in olivines of most primitive basalt from the nearby Mount Caraïbes massif (N. Métrich, unpub. data, pers. comm. 2012), taken as analogue of La Soufrière feeding basalt.

^b Dissolved H₂O, S, Cl and CO₂ contents of rhyolitic melt inclusions entrapped in pyroxene and plagioclase phenocrysts of La Soufrière andesites (Semet et al., 1981; Poussineau, 2005; Boudon et al., 2008).

^c Bulk exsolution rate = $1 - [(X_i/\text{K}_2\text{O})_r / (X_i/\text{K}_2\text{O})_b]$, where X_i is the respective concentration of each volatile in the rhyolitic (r) and basaltic (b) melts.

^d CO₂ content in the feeding basalt (this work) was estimated from the CO₂/S ratio of SC fumarolic fluid and the bulk amount of degassing basaltic melt (~1400 m³ d^{−1}) inferred to supply the fumarolic flux of sulfur, assumed to be magmatic in origin (see text for explanation).

elemental sulfur emitted in 2012 from SC vent (2.64 t/d) and supplied to Tarissan crater (1.5 t/d after correction for scrubbing, Section 5.1), its scaling to the bulk amount of S exsolved in the system implies a magmatic gas supply from $4 \times 10^6 \text{ kg d}^{-1}$ or $1400 \text{ m}^3 \text{ d}^{-1}$ ($0.016 \text{ m}^3 \text{ s}^{-1}$) of basaltic melt with a density of 2800 kg m^{-3} . Due to uncertainty on the fumarolic sulfur flux (25%, Section 5.2) and other variables (K_2O , S), this estimate is probably accurate to within 30–35%. Such a relatively small rate reflects the modest gas fluxes from La Soufrière despite its current degassing unrest.

When referred to the above estimate, the total fumarolic flux of magma-derived carbon dioxide from SC and TAS vents in 2012 (15 t/d) constrains a bulk exsolved amount of 0.4 wt.% CO_2 in the magmatic system. Since carbon dioxide exsolves still earlier than sulfur during basalt degassing and is at the detection limit in rhyolitic melt inclusions of La Soufrière andesite (Poussineau, 2005), this amount should well approximate the original CO_2 content of the parental basalt (Table 5). In fact, it falls within the typical CO_2 range for arc basaltic magmas (Wallace, 2005). Including carbon dioxide, the feeding system may thus contain ~1.3 wt.% of total exsolved gas whose molar composition, on top of the reservoir (~160 MPa), would average ~74% H_2O , 17% CO_2 , 6% S and 3% Cl (Table 5). We compute that the escape of this magmatic gas phase from the equivalent of $1400 \text{ m}^3 \text{ d}^{-1}$ of basalt beneath La Soufrière can provide a magmatic flux of 28 t/d of H_2O and 2.5 t/d of chlorine. Comparing with the fumarolic emission rates of H_2O (~200 t/d) and Cl (1.1 t/d) in March 2012 (Table 3), we verify the following two points: (a) an extensive (7 times) meteoric dilution of the magmatic water prior to reaching the surface, which fully agrees with isotopic data for the fumarolic steam (Benauges, 1981; Brombach et al., 2000; Allard, 2006) and with the much more hydrous composition of SC fumarolic fluid (~97% H_2O) compared to the reservoir-derived magmatic gas (Table 5). Such a feature is well accounted for by the huge tropical rainfall rate of ~10 m per year on top of La Soufrière, a great part of which infiltrates into the volcanic edifice (Villemant et al., 2005); and (b) a substantial removal of the magma-derived chlorine by dissolution in La Soufrière hydrothermal aquifers, in good agreement with elemental balances (Section 5.3) and Cl isotope data (Li et al., 2012).

6. Conclusions

Based on in situ plume measurements and gas analysis at La Soufrière de Guadeloupe in March 2006 and March 2012, we provide the first direct estimate of steam and gas emission rates from the summit fumarolic activity of this volcano during a period of degassing unrest. We find a total gas release of ~80 tons/day in 2006 and ~220 tons/day in 2012, most of which as steam, whose temporal increase is consistent with enhanced degassing activity and the reactivation of new vents. Including thermal water outflow and diffuse soil degassing, mass balance calculations show that summit fumarolic degassing contributes most of the volatile budget of La Soufrière and most of its thermal output, evaluated as about 8 MW in March 2012. Heat output from the hydrothermal manifestations widely exceeds the energy released by contemporaneous seismic activity.

MultiGAS analysis of H_2O , CO_2 , H_2S , SO_2 and H_2 plume emissions from the different summit vents of La Soufrière, performed for the first time, allows us to define a common fluid end-member that is emitted almost unmodified at the most active South Crater (SC) but variably affected by shallow secondary alterations at other vents. As shown by isotopic data, this fluid contains magma-derived helium, CO_2 and Cl, likely released from the magma reservoir confined at 6–7 km depth beneath the volcano. An ultimate magmatic derivation of sulfur is also likely, whereas H_2O originates predominantly from the boiling of meteoric groundwater. Based on this information, on petro-geochemical data for La Soufrière magmas and their dissolved volatile content, we have tentatively assessed the amount of basalt feeding La Soufrière magmatic system whose underground degassing is needed to supply the current volcanic gas fluxes. Assuming a magmatic derivation of sulfur, we find

that the release of free magmatic gas derived from about $1400 \text{ m}^3/\text{day}$ ($\pm 30\text{--}35\%$) of feeding basalt could well account not only for the gas fluxes measured in March 2012, but also for the isotopic composition and the specific chemical behaviour of each volatile species upon interaction with the hydrothermal system. Comparing the volcanic fluxes of H_2O and Cl with the potential magmatic gas supply from depth verifies both extensive meteoric dilution of the magmatic water and substantial scrubbing of magmatic chlorine in the hydrothermal system, in good agreement with isotopic data and chemical balances.

Our present estimate of the rate of magmatic gas release from the feeding system of La Soufrière is the very first one to be quantified from volcanic gas flux measurements. Given its assumptions and uncertainties, this estimate will have to be refined in future based on improved knowledge of the volcano plumbing system. Since the gas and heat budget of the volcano is one key indicator of its level of activity, we recommend that regular gas flux survey becomes undertaken at La Soufrière, in complement to routine gas sampling and analysis. Such a survey should permit to quantify temporal changes in the mass balance between underground magma degassing and hydrothermal supply to the surface emissions, and hence to better distinguish the precursory signals of a forthcoming magmatic eruption from temporary dynamic changes in the hydrothermal system. Automated MultiGAS monitoring already conducted on several volcanoes worldwide (Aiuppa et al., 2011) demonstrates its great potential for continuous gas survey of a dormant volcano such as La Soufrière. Combining such a survey with periodic MultiGAS measurement of the volcanic plume discharge, as described in this study, would thus open new perspectives for improved monitoring and forecasting of La Soufrière behaviour in future.

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