Remote and in situ plume measurements of acid gas release from La Soufrière volcano, Guadeloupe

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Abstract

This paper presents the first remote measurements of La Soufrière gas emissions since the fumarolic and seismic reactivation in 1992. The chemical composition of the plumes has been measured from May 2003 to September 2004 using an Open Path Fourier Transform InfraRed (OP-FTIR) spectrometer, up to 15 m downwind the South Crater. HCl is clearly detected (concentration between 2.4 and 12 ppmv) whereas SO_2 and H_2S generally remain below the detection limit of the OP-FTIR. Direct measurements of SO_2 and H_2S near the South Crater with a Lancom III analyzer show a fast decrease of their concentrations with the distance. Calculated Cl/S mass ratios are high: from 9.4 ± 1.7 at 15 m from the vent to 2.8 ± 0.6 at 140 m. The enrichment in HCl of the gas emitted at La Soufrière, observed since 1998, corresponds to the degassing of a magma enriched in Cl and depleted in S. This result agrees with isotopic measurements which suggest a magmatic origin of the gases. Readjustments inside the volcanic system may have taken place during the seismic activity beginning in 1992 and enhance the transfer of magmatic gases to the summit.
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1. Introduction

Since the last magmatic eruption of 1440 AD, La Soufrière of Guadeloupe, an andesitic stratovolcano located in the subduction arc of the Lesser Antilles, has undergone at least four phreatic eruptions (Boudon et al., 1988, 1989; Komorowski et al., in press), the last of which was in 1976–1977. A stream-and-ash column rose above the summit in July 1976. The eruption lasted eight months and consisted of 26 phreatic explosions. After May 1977, the fumarolic activity decreased gradually and was further reduced between 1984 and 1992. Only small peripheral fumaroles were observed.

In 1992, the fumarolic activity resumed (Zlotnicki et al., 1994; Komorowski et al., 2001): and three volcanic plumes rose above the summit. The strongest one is emitted from the South Crater (CS). A substantial increase in shallow seismic activity accompanied this reactivation. Since 1992, the alert level is "yellow" (vigilance). The fumarolic activity has progressively extended toward the North–North-West, with a reacti-

vation of the Tarissan (TAS) vent in 2000 and the Napoléon (NAP) vent in 2002.

Since 1976, gas chromatography (GC) analyses have been regularly performed. In 1997, GC analyses on samples from the CS vent showed that: (1) the most abundant gas released was water vapor (97–98% of the total volume); (2) the other main components were CO_2 (~85% mol), H_2S (~9% mol) and three diatomic gases: H_2, N_2, and O_2 (respectively, ~2.5%, 2.7%, 0.8% mol); (3) SO_2, HCl as well as CO were below the detection limits of the gas chromatograph.

In 1998, gas emanating from the main summit plume CS suddenly became very acid. The pH reached values close to 1, as opposed to 4 to 5 before. Tiny acid droplets and important solid sulfur deposits have been observed at the summit, near the CS.

The strong reactivation of the fumarolic activity at the summit and the remarkable change in chemical parameters are not associated with significant variations of the other important monitoring parameters such as seismic activity at depth, large scale ground deformation, and higher gas temperatures. Average gas temperatures remained around 105 °C. However, many catastrophic volcanic events are related to explosive activity on apparently dormant volcanoes (e.g., Montagne Pelée 1902, Mount St. Helen 1980, Pinatubo 1991, Soufrière Hills 1995). As a consequence, any attempt to understand an increase in volcanic activity in quiescent systems deserves attention.

The persistent degassing, the origin of the high acidity of gas emissions at La Soufrière of Guadeloupe and the source mechanisms of this reactivation are poorly understood. HCl concentration seem to be a key parameter. Unfortunately, the acidity made direct sampling and pH measurements unsafe since 1998, and gas chromatography is not suitable to study HCl behavior. Thus, a necessity for new tools has emerged. Correlation spectrometer (COSPEC) is widely used to monitor SO_2 during volcanic eruptions (Hoff and Millan, 1981; Stoiber et al., 1983). However, SO_2 measurements are not sufficient for the full understanding of the degassing mechanisms. Consequently, in the last ten years the remote sensing technique of Open Path Fourier Transform Infra Red spectrometry (OP-FTIR) has been widely used to monitor chemical composition of gases on different volcanoes: Unzen and Aso, Japan (Mori et al., 1993; Mori and Notsu, 1997), Galeras, Colombia (Stix et al., 1993), Masaya, Nicaragua (Horrocks et al., 1999; Burton et al., 2000; Duffell et al., 2003), Vulcano, Italy (Francis et al., 1995; Mori et al., 1995), Popocatépetl, Mexico (Goff et al., 2001), Stromboli, Italy (Burton et al., 2001);

Oldoinyo Lengai, Tanzania (Oppenheimer et al., 2002), Soufrière Hills, Montserrat (Oppenheimer et al., 1998a,b,c,d; Edmonds et al., 2002), Etna, Italy (Francis et al., 1995; Burton et al., 2003; Allard et al., 2005). Thus, experience increases and the use of OP-FTIR becomes easier.

In order to better understand the volcano dynamics and provide critical information for evaluating hazards at La Soufrière, Guadeloupe, we undertook OP-FTIR measurements of volcanic plumes. In this paper we present OP-FTIR data and LANCOM III gas analysis collected between May 2003 and September 2004 at the summit of La Soufrière. In the discussion we focus on HCl/SO_2 ratios in order to give some new insights on the origin of the ongoing degassing at La Soufrière.

2. Two new tools to monitor La Soufrière gases: the OP-FTIR and the Lancom III gas analyzer (LIII)

2.1. OP-FTIR

We used a MIDAC Corporation OP-FTIR spectrometer which incorporates a Michelson interferometer attached to a 25 cm Newtonian telescope (Fig. 1) with a mercury–cadmium–telluride (MCT) detector or an ad-
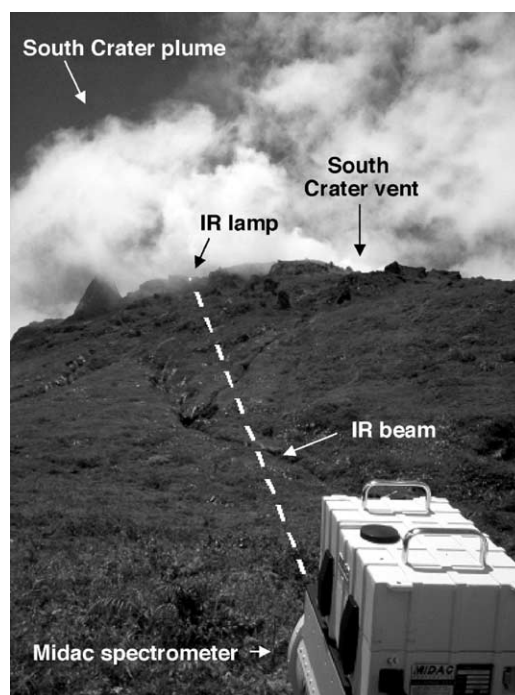

Fig. 1. Example of OP-FTIR measurement on April 15, 2004 at La Soufrière of Guadeloupe. The spectrometer was located at the 'Savane à mulets' parking and the infrared lamp on the crater rim (light spot).

ditional indium–antimonide (InSb) detector. The detector is cooled at 77°K with liquid nitrogen. The optical telescope allows measurement of a target gas located at a distance of few meters to several km away. The OP–FTIR analyzes several gases simultaneously since it measures all wavelengths of light in the range 4500–500 cm^{-1}. In this study we used the spectrometer with artificial infrared sources: two different SiC glow-lamps (12 V DC power), placed at the focus of a 50 cm diameter parabolic reflector. OP-FTIR could be used when volcanic activity become high or during eruptions. In these cases, natural infrared emitting sources like the Sun, hot lava or gases, may be used. As the plume passes through the infrared beam, molecular components (of the plume) absorb some characteristic frequencies. These absorptions are recorded in the form of an interferogram (detector signal as a function of mirror position) which is converted by Fourier transform into a single beam spectrum, using a commercial software (AutoQuant Pro, Midac Co.).

Instrument control, data storage and analysis were performed with a notebook computer. In the retrieval process of gas composition, each single-beam spectrum is compared to a 'reference' spectrum (background) corresponding to a sample 'without plume' and the data are converted into absorbance spectra. For each set of measurements, the background was chosen as the spectrum containing the smallest amount or no volcanic gas, within the same set. Background spectra were collected when the wind carried the plume out of the measurement path. Compositions of the plume were estimated by comparison of field absorbance spectra with reference spectra of several gas components measured in laboratory with the same equipment. We use the Midac 'Standards' library and a non-linear least-squares fitting procedure (AutoQuant Pro, Midac Co.). The retrieval output consists in 'column amounts' of target gases in parts per million (volumetric) per meter (i.e., ppmv m). We need to estimate the width of the column actually crossed by the volcanic gases to deduce the gas concentrations in ppm.

A more detailed description of OP-FTIR data reduction procedures may be found in Francis et al. (1995) and Oppenheimer et al. (1998b).

2.1.1. Main experimental difficulties at La Soufrière

We met three main difficulties during the first campaigns in OP-FTIR measurements at La Soufrière:

(1) *The weather (humidity, clouds and wind)*: At the summit of this tropical volcano (1467 m above sea level), clouds often cover the summit and rain fall is high (between 300 and 1000 mm per month). Thus, temporal windows for OP-FTIR measurements under good meteorological conditions are exceptional (Fig. 1). The humidity is high, between 80% and 100%, higher during the night (~100%). The smallest values are observed around midday (data OVSG, 2003–2004). Consequently all our measurements were made between 10:00 pm and 4:00 am. Nevertheless, the OP-FTIR spectra are largely contaminated by atmospheric water vapor. Wind velocity and direction are also parameters that need to be accounted for.

(2) *The volcano morphology*: On Fig. 2, three distinct points for the South Crater CS emit gases: the north one (CSN) which is more active than the south one (CSS) by many orders of magnitude

Fig. 2. View of the South Crater vents and details on the emission points: CSS, CSC and CSN (Photo by M. Feuillard, 1992).

and a very small central point (CSC). For all OP-FTIR measurements, the infrared source was established at the summit in the SW sector, near the CS rim over which the CS plume generally passes. The source was carried by hand to the summit over more than one kilometer. The slope of the volcano flanks is sharp (55° on average). Passive experiments using the Sun as an infrared source would be difficult at La Soufrière since there is no place corresponding to such configuration accessible by car.

(3) *Acidity of gases*: We limited the monitoring activities to few hours since corrosion due to the acidity of gases at the summit can seriously dam-

age the instruments, particularly the mirror surfaces coated with Zn–Sn of the IR lamp.

In conclusion, we had to stay for many hours on many days to obtain good measurement conditions. The presented datasets have been obtained during periods of one to three hours.

2.1.2. Operating mode for La Soufrière

We measured infrared absorption across an atmospheric path of 640 ± 5 m (May 31, 2003; April 15, 2004; September 17 and 25, 2004) and 690 ± 5 m (April 9, 2004) between the infrared source and the detector (Fig. 3). We used GPS positions of the source,
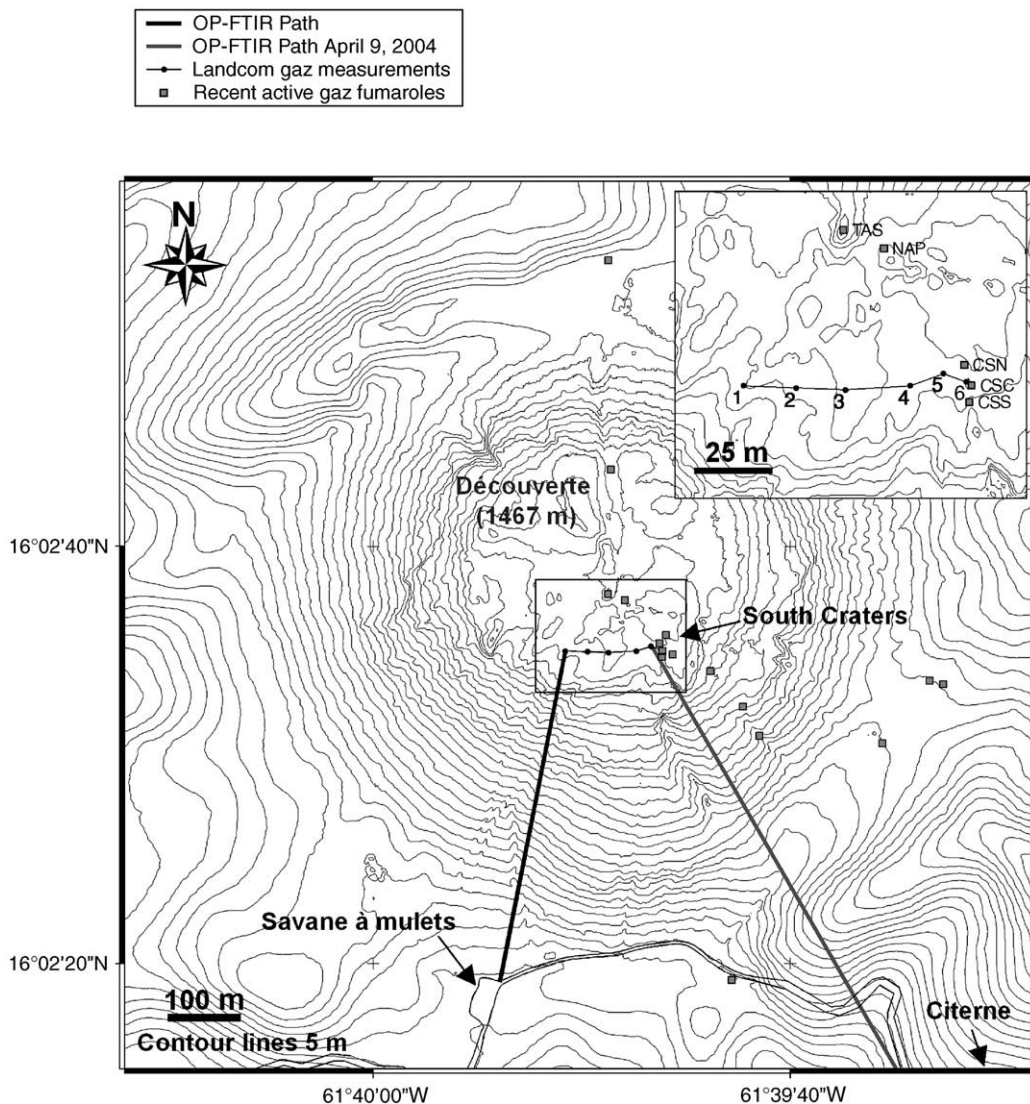

Fig. 3. La Soufrière dome. The lines correspond to the two OP-FTIR paths used to study the South Crater (CS) plume emitted from the CS vents (CSN, CSC, CSS). TAS and NAP correspond to Tarissan and Napoléon vents. The Lancom III profil carried on the September 25, 2004 along the plume is also reported.
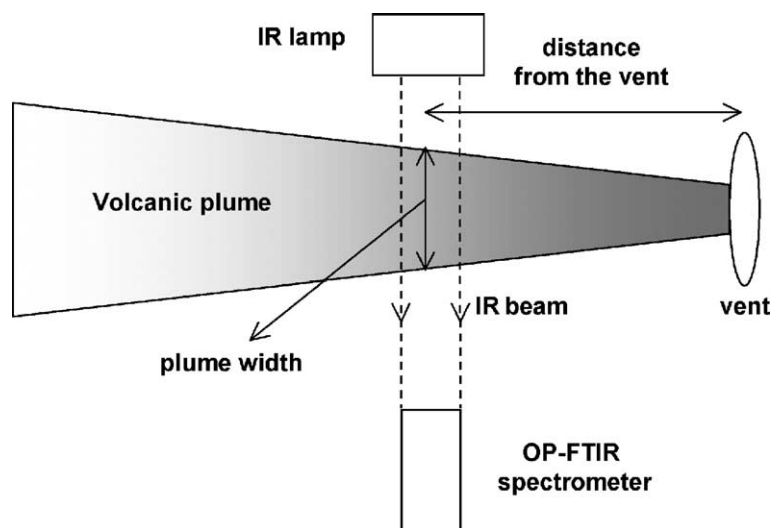
Fig. 4. OP-FTIR measurement configuration used at La Soufrière. The infrared beam crossed the South Crater plume at 15 m (dataset 2) or 140 m (other datasets) from the vent.

the receiver and the vents to estimate the above slanting distances. In all configurations except on April 9, 2004, the beam crossed the plume at 140 ± 1 m from the two main emission points of the South Crater (East wind). The corresponding observed plume width (Fig. 4) varies between 0 and 35 (± 5) m. The variability of the plume width is essentially due to the changes in the wind intensity and direction (OVSG data). In the second campaign (April 9, 2004), due to the South–East wind direction, the spectrometer and the infrared source were aligned across the South Crater, so that the plume has been sampled closer the vent (15 ± 1 m). The corresponding observed plume width was nearly constant, around 25 ± 5 m. Only a part of the plume, essentially from the CSS emission point, was sampled.

Signal to noise ratios were improved by co-adding 16, 32 or 64 consecutive scans (2 s per scan) and all data were acquired at a spectral resolution of 0.5 cm^{-1}. During the last campaigns in September 2004, since fast variations in wind direction tend to carry the plume aside the IR source, we chose to co-add only 16 scans.

In order to warrant the effect of overlapping water bands on our analysis, we limit our research to the spectrum-lines of the volcanic gases of interest (SO_2, H_2S, HCl, HF, CO_2, CH_4, CO, COS and SiF_4) located out off strong water bands. Note that water vapor absorption is strong in 1200–2000 cm^{-1} and 3400–4100 cm^{-1} ranges. The spectral windows used in our analysis method are given in Table 1. Elemental gases such as Ar, and diatomic gases such as H_2, O_2 and N_2

Table 1

Gas selected spectral regions in the OP-FTIR analysis method, the chosen detectors and the detection facility

Gas	Selected spectral analysis range	Detector	Overlapping H_2O	Detection facility
HCl	2894–2713 cm^{-1}	MCT	No	Easy
SO_2	1257–1068 cm^{-1} (weak)	MCT	No	Easy at high concentration
	1410–1300 cm^{-1}	MCT	Yes	Difficult
	2525–2464 cm^{-1} (very weak)	InSb[a]	No	Difficult
H_2S	2740–2638 cm^{-1} (weak)	MCT	No	Difficult
	1400–1000 cm^{-1}	MCT	Yes	Difficult
HF	4211–3985 cm^{-1} (strong)	MCT	No	Easy
CO_2	2283–2238 cm^{-1}	MCT/InSb	No	Strong absorption lines saturating the detector. Need a specific analysis.
CO	2275–2000 cm^{-1}	MCT/InSb	No	Not easy at small concentration
COS	2105–1979 cm^{-1}	MCT	No	Quite easy
CH_4	3026–2878 cm^{-1}	MCT	No	Easy
SiF_4	1079–958 cm^{-1}	MCT	No	Quite easy

[a] InSb detector is sensitive over a narrow frequency band, 3000–1600 cm^{-1}.

do not absorb infrared radiation and therefore are excluded of the analysis.

2.2. Lancom III portable gas analyzer

2.2.1. Instrument description

We used a portable (less than 6 kg) gas analyzer Lancom III (LIII) that allows to simultaneous measurement of up to 4 gases (SO_2, H_2S, CO_2 and CO). Two different sensors (Table 2) are used to measure the concentrations. The gas sample is drawn through a 3 m sample probe. The sample enters the water catchpot where residual water is removed. The sample gas is then passed through a 0.1 μm particles filter. After removing flow and pressure variations, the gas is routed to the sensor manifolds. To warranty their accuracy, the sensors are purged with fresh air each time the analyzer is switched on or off and are calibrated with ambient air at startup.

2.2.2. Protocol of measurements

The gas concentrations of SO_2, H_2S, CO_2, and CO have been measured at the summit of La Soufrière along the plume (Fig. 3) using LIII. All measurement points are located by GPS. The measurements have been done walking East towards the South Crater vent over a distance of 140 m, on September 25, 2004. The weather was particularly fine: very clear sky, humidity < 80% (Table 3). From time to time, the wind took a more southern component and then made simultaneous OP-FTIR measurements possible. The first point measured with LIII was located near the infrared source of the OP-FTIR. For each profile point, the analyzer continuously monitored during 10 min (one measurement per minute) and we chose to register the higher detected value.

3. Results

Over the investigation period at La Soufrière, between May 2003 and September 2004, we collect more than 400 OP-FTIR spectra divided in 6 datasets. For each spectrum, we calculate column amounts (in ppmv m) of the gas present in the plume. Then for each dataset we compute the average gas column amounts, using the reliable values (95% confidence). They are presented in Table 3 as well as the standard deviation and the range of reliable amounts. Gas species retrieved from OP-FTIR spectra include HCl, SO_2, CH_4 and SiF_4. H_2S, HF, CO and COS remain undetected. Due to uncertainties in the choice of background spectra, the precision on the gas column amounts varies between 10% and 20%. The variability in gas concentrations in a same dataset can be important since the width of the plume really crossing the infrared beam varies.

Due to the used IR path configurations, the reported values represent the plume composition at two given distances, 15 and 140 m, from the CS vent (Fig. 4). This choice allows us to compare the OP-FTIR results to the point measurements carried out along the plume using the LIII analyzer.

3.1. HCl

HCl is easily detected since its concentrations reaches high values and its absorbance peaks can be distinguished from those of water vapor (Table 1). The average column amount of HCl falls in the range 50 to 303 ppmv m (Table 3). Fig. 5 shows a comparison of HCl peaks in a field spectrum with a laboratory reference spectrum of HCl. For the datasets (1, 3, 5), the distance from the source was nearly 140 m and the results are consistent: the average HCl values are slightly the same, near 110 ppmv m. For dataset 3 we find a higher average amount of 153 ppmv m attributed to the observed larger width of the plume. It is interesting to compare these results to dataset 2 where the CS emission points were very near the IR source (15 m). We measure higher HCl amounts in dataset 2 (206 ppmv m) compared to the others. Since we only measured part of the CS emission (CSS) the total HCl amount at such a distance may be much higher.

Table 2
Lancom III gas analyzer: sensor types and measurement specifications

Gas	Sensor type	Standard range	Max. range	Accuracy	Resolution
Sulphur dioxide, SO_2	Electrochemical	0 to 2000 ppm	0 to 5000 ppm	± 2%	± 1 ppm
Hydrogen sulphide, H_2S	Electrochemical	0 to 200 ppm	0 to 1000 ppm	± 2%	± 1 ppm
Carbon dioxide, CO_2	Infrared	0 to 25.0% vol.	–	± 0.5% vol.	± 0.1% vol.
Carbon monoxide CO low[a]	Electrochemical	0 to 2000 ppm	0 to 4000 ppm	± 2%	± 1 ppm
Flue gas temperature		Thermocouple		Measured 0 to 1000 °C ± 5 °C)	
Ambient temperature		Standard		Measured over operating range	
Flow (velocity)				1 to 50 m/s	

[a] CO is H_2 compensated.

Table 3
Column amounts of gas and HCl/SO$_2$ molar ratios retrieved from active OP-FTIR measurements between May 2003 and September 2004 at La Soufrière, Guadeloupe.

La Soufriere, Guadeloupe-OP-FTIR data												
	HCl	SO$_2$	CO	COS	SiF$_4$	CH$_4$	(HCl/SO$_2$)$_{av}$	HCl$_{av}$/SO$_{2av}$	pH[a]	T_{gas}[a] °C	HR[b] %	V_{wind}[b] km h^{-1}
			ppmv m									
Dataset 1:31/05/2003 1120–1221 h spectra MCT 32–64 scans LAMP1[c]												
Range	45–180	7–23			0.9–1.4	342–387	6–14		0.0–0.6		96–100	33–39
Average	114	12	nd	nd[d]	1	373	11.8	9.5		98	99.4	35.6
Stand. dev.[d]	40	4			0.2	13	2.5				1.6	2.2
Dataset 2: 09/04/2004 1100–1230 h 54 spectra MCT 64 scans LAMP2[c]												
Range	150–301	4–6			1–2	183–416	26–54		0.4–0.7		67–76	11–17
Average	206	5	nd	nd	1.7	273	40	41.2		109.3	68.4	13.8
Stand. dev.	39	1			0.2	52	7				3	1.5
Dataset 3: 15/04/2004 1100–1300 h 82 spectra MCT 32 scans LAMP2												
Range	56–303	5–20			1.9–2.2	226–773	14 max		0.4–0.7		78–94	9–24
Average	153	13	<25	nd	2	544	–	11.8		109.3	90.6	13.5
Stand. dev.	68	14			0.07	98					5.1	3.8
Dataset 4: 17/09/2004 1435–1520 h 34 spectra InSb 32 scans LAMP2												
Range	45 max					251–307			0.9–1.1		93–97	22–30
Average	<50	nd	<10	nd	nd	279	–	–		101	94.8	25
Stand. dev.						14					1.7	3.4
Dataset 5-1: 25/09/2004 1020–1240 h 175 spectra Insb 16 scans LAMP2												
Range	71–143					207–404			0.9–1.1		67–78	9–16
Average	102	nd	<25	nd	nd	280	–	–		101	74.2	13.4
Stand. dev.	22					25					2.9	1.7
Dataset 5-2: 25/09/2004 1400–1430 h 46 spectra MCT 16 scans LAMP2												
Range	70–156	8–14			2–2.4	362–426	6–12		0.9–1.1		69–82	10–21
Average	112	12	<20	nd	2	394	9.2	9.3		101	73.9	13.4
Stand. dev.	32	1.1			0.2	16	2				5.8	4.9

[a] pH and gas temperature, T_{gas}, measurements at the South Crater (SC) vent (data OVSG-IPGP, 2003–2004).

[b] Relative humidity, HR, and wind velocity, V_{wind}, from the meteorological station, Piton Sanner (data OVSG-IPGP, 2003–2004), during OP-FTIR measurement intervals.

[c] The infrared lamp LAMP2 is more powerful than LAMP1.

[d] nd=non-detected; stand. dev.=standard deviation.

3.2. SO$_2$ and H$_2$S

For OP-FTIR measurements, we use the spectral ranges indicated in the protocol of Table 1. For SO$_2$, using three different bands and two detectors, we always find low column amounts (<23 ppmv m) and H$_2$S is undetected. Using a mean plume width of 25 m for the OP-FTIR, we compared these results to those with LIII measurements. Fig. 6 shows that the concentrations of H$_2$S and SO$_2$ measured using LIII gas analyzer, decrease when the distance from the South crater increases. H$_2$S is the dominant sulfur gas specie.

At 15 m from the CS vent, the LIII measured at a point situated near the center of the main emission point (CSN) whereas OP-FTIR measured the weaker plume from CSS. Then, it is not surprising that LIII yields a value of 3 ppm for SO$_2$, higher than the 0.2 ppm calculated with a 25 m plume width from OP-FTIR. As for HCl and SO$_2$, we can assume that H$_2$S measured by the OP-FTIR at 15 m from the vent is smaller than that measured by LIII. This agrees with the smaller flow from CSS.

H$_2$S/SO$_2$ ratio is close to 2 at the vent. This result is consistent with the Observatory measurements on CS gas samples using chromatography, prior to 1998. H$_2$S and SO$_2$ concentrations in dry gas range respectively from 5% to 15% and 0% to 1%, leading to H$_2$S/SO$_2$ ratio larger than 1.

At 140 m from the vent, SO$_2$ concentration falls below the LIII detection limit for SO$_2$ (1 ppm) and H$_2$S is less than 2 ppm. Fig. 6 also suggests a rapid
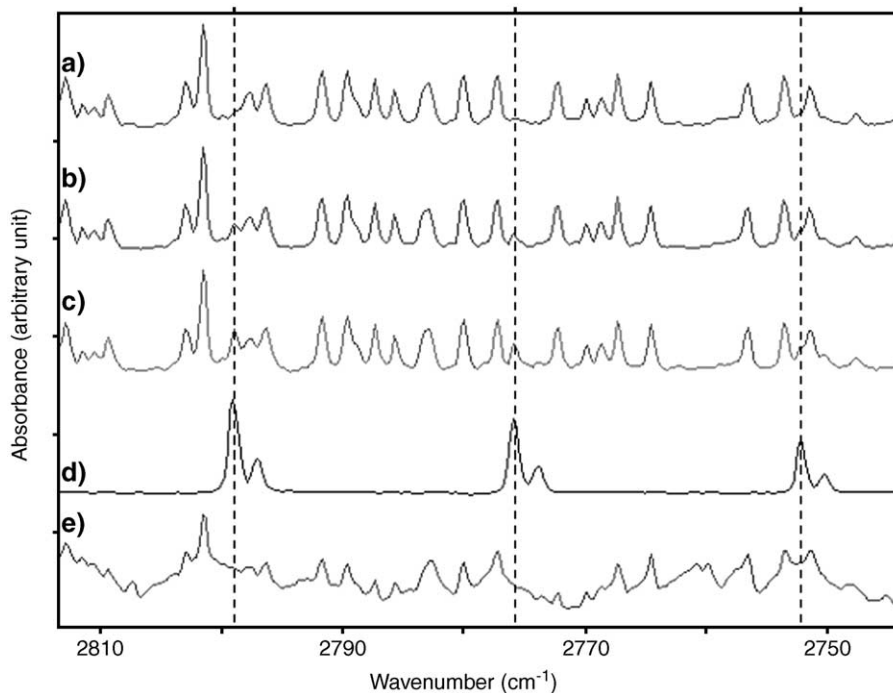
Fig. 5. Comparison of HCl absorbance lines of three field spectra collected on September 25, 2004 with a laboratory spectrum of HCl: a) sample #13(0 ppmv m of HCl), b) sample #1 (60 ppmv m), c) sample #25 (160 ppmv m), d) laboratory reference of HCl, e) atmospheric water spectrum measured in the field along the Citerne road, near the volcano. Resolution: 0.5 cm^{-1}.

vanish of both H_2S and SO_2 near the vent. At 140 m from the CS vent, OP-FTIR and LIII results are in agreement for SO_2 and H_2S.

3.3. Other gases

(1) CO_2 absorbance peaks are largely present in the OP-FTIR spectra and result from atmospheric and volcanic contributions. In the recorded spectra the very high absorbance peaks of CO_2 are truncated due to detector saturation along the 640 or 690 m IR beam and CO_2 could not be measured. We conclude that the detector gain adapted to measure all other gas was too high to simultaneously recover CO_2 concentration. The maximum CO_2 concentration measured with LIII near the vent is around 1700 ± 1000 ppm. Since the mean atmospheric CO_2 concentration is about 370 ppm we consider that these CO_2 measurements are not reliable.
(2) CO is generally not detected by OP-FTIR. This result is consistent with LIII measurement since we measure 0 ± 1 ppm for all points.
(3) COS is also below OP-FTIR detection limit.
(4) On May 31, 2003 OP-FTIR measurements over 25 m of atmosphere at the 'Savane à mulets'

parking (~1142 m alt.) gave a concentration of 0.6 ppm for CH_4. This value is lower than the average atmospheric CH_4 concentration, 1.7 ppm. Using the measured atmospheric CH_4 concentration we estimated an atmospheric CH_4 column
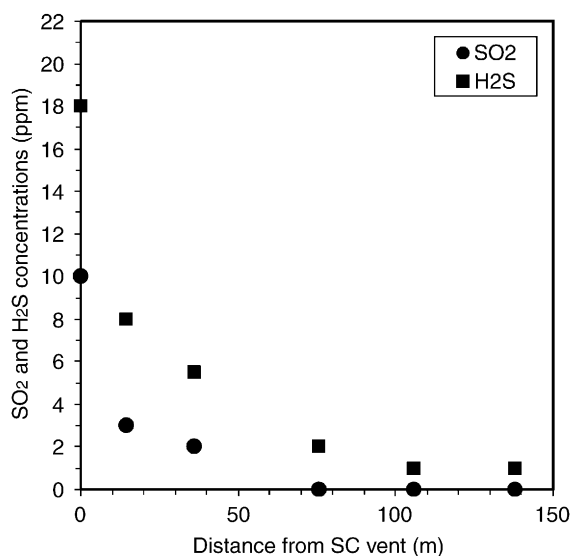

Fig. 6. Variation of SO_2 and H_2S concentrations measured using the Lancom III gas analyzer with the distance from the South Crater vent.

amount of 380 ppmv m for a total column length of 640 m. The total column amounts we measured over La Soufrière range from 280 to 544 ppmv m. The higher CH_4 value in dataset 3 is correlated to a higher value of HCl column amount compared to the other datasets. This indicates the presence of volcanic CH_4.

(5) SiF_4 is present in datasets 1, 2, 3 and 5 in concentration smaller than 2.4 ppmv m. SiF_4 is a trace component of fumarolic gases on volcanoes arising from the fast interactions between magmatic HF and wall rocks. This explains why HF had not been detected.

4. Discussion

4.1. Gas composition

4.1.1. HCl

HCl was quantified reliably using the OP-FTIR techniques. Results show that the HCl column amount can reach 300 ppmv m even at 140 m from the vent. Assuming a plume width of 25 m, this column amount corresponds to HCl concentrations of 12 ppmv, which is large compared to other volcanoes (Oppenheimer et al., 1998b). This confirms the very high acidity of the gas at the summit and the necessity to limit human access to the summit. Note that the health and safety norm for a 10 min exposure to HCl is 5 ppmv.

Since the average gas temperature, 105 °C, measured by inserting a temperature sensor into the South crater vent, is constantly close to saturated water vapor, water droplets are present in the plume. As a result, a large part of the HCl molecules coming from the vent are dissolved in water owing to the high solubility of HCl. The OP-FTIR spectrometer only measures the remaining HCl molecules in the plume and not the ions H_3O^+ and Cl^-. Thus the real concentration of HCl at the source (CS vent) should be consistently higher than the 8 ppmv mean concentration measured on April 9, 2004, near the CS vent (15 m).

pH measurements were used to estimate HCl concentration at the CS vent. The pH is measured in gas condensates obtained by putting at the CS vent a cold plate on which fumarolic steam condenses. pH values are between 0 and 1 (Table 3). These pH values allow us to approximate the amount of HCl dissolved in the plume water droplets near the vent, since HCl is the strongest present acid. That means that nearly all H_3O^+ present in the droplets come from HCl. For pH=1, there is 0.1 mole HCl for 55 liquid water moles. Since the fumarolic steam is essentially constituted of water (at 99%) the concentration of HCl in the vent is close to 0.1/55 or 1820 ppm. For lower pH, this concentration is higher. The OP-FTIR measurements provide smaller HCl concentration at the CS vent. Close to the vent, a rapid dissolution of HCl in water droplets may be responsible for the lower measured HCl concentration. This conclusion is related to measurements on gas condensates sampled between 1998 and 2003 at the South Crater. Gases were collected directly from the vent in a refrigerated vessel and analyzed by ion chromatography (G. Hammouya, N. Jendrzejewski and P. Agrinier, personal communication). The results show high values and temporal variations in chlorine concentrations which range between 16 and 1340 mmol l^{-1} (or 0.03–2.4 10^4 ppmv). The highest value had been measured in May 2001, with a pH=0.25.

Important dissolution in water droplets at the CS vent exit seems to be the main mechanism responsible for the small HCl concentrations measured in the plume, even at 15 m from the vent. Close to 100 °C, the HCl solubility in water is about 15 mol l^{-1}. The high contents of HCl in water droplets contained in the plume is later responsible for the complete destruction of the vegetation even at 200 m from the vent below the plume region. Free HCl molecules also attack the plants. Moreover a boiling pond of extremely acid water (pH is between −1 and 1) at the summit acts as a trap of acid volatiles.

Further, between 15 and 140 m from the vent, the high air humidity and the mixing of the plume with ambient air may be responsible for the small HCl decay observed on OP-FTIR measurements.

An explanation for high Cl in volcanic fumaroles without eruption could be assimilation and volatilization of a shallow seawater source of chlorine. Symonds et al. (1990, 1992) explain that Cl-rich gases observed at Mount St. Augustine volcano (Alaska) in 1987, on andesitic lava-dome and in post-eruptive fuming state, is partly due to interaction between seawater and magma at shallow depth (less than 3 km). Components of both magmatic and seawater origin are also present in Vulcano fumaroles (Chiodini et al., 1993). Isotopic studies by N. Jendrzejewski (pers. comm.) show that a strong increase of chlorine concentration measured in May 2001 on condensates from La Soufrière is associated with an important increase in $\delta^{37}Cl$. This is incompatible with direct seawater input to the volcanic system at shallow depth.

In conclusion, spectroscopic remote measurements, even if they only measure a small proportion of the total emitted HCl, should detect any variation in fumarolic

emissions at La Soufrière. Regular OP-FTIR measurements of HCl are therefore necessary at the summit.

4.1.2. SO_2 and H_2S

We observed that SO_2 and H_2S decrease with increasing distance from the vent. Different processes are proposed to explain such a behavior (Mori et al., 1995; Symonds et al., 1994, 2001):

(1) Since we observed an important solid sulfur deposit around the CS vent, reactions between sulfur compounds of the plume can partly consume the SO_2 and H_2S at the emission point: $2H_2S + SO_2 \rightarrow 3S + 2H_2O$.

(2) A part of SO_2 and H_2S are dissolved in liquid droplets of the plume. The partition is complex and depends upon factors such as temperature and pH. However SO_2 and H_2S have relatively low solubilities in water: 0.1 mol l^{-1} at 100 °C for SO_2 and a little less for H_2S.

(3) Atmospheric oxidation of the sulfur components can modify the plume composition. A great part of H_2S can be oxidised to give SO_2 whereas SO_2 can be converted to sulfuric acid, H_2SO_4, by oxidation processes. The solubility of $H_2SO_4(g)$ in water is very high. Consequently dissolution in water is a possible process removing the sulfur species from the plume, despite the low solubility of SO_2 and H_2S.

(4) We measured the gases after their emission and mixing with air. Important local winds, up to 40 km h^{-1} during our study, can efficiently disperse the gases. Then physical dilution of the plume in ambient air may be another process responsible for the lowering of SO_2 and H_2S concentrations in the plume.

4.2. HCl/SO_2 ratio at the South Crater vent

In order to discriminate the mechanisms responsible for the degassing at La Soufrière, we tried to quantify the HCl/SO_2 ratios for each OP-FTIR spectrum. It was not always possible due to the lack of net absorption peaks for SO_2. In Table 3 we give the average values of such calculated ratios, $(HCl/SO_2)_{av}$, with their standard deviation. We also give the ratio of average HCl to the corresponding average SO_2 for a given dataset, HCl_{av}/SO_{2av}. The two types of ratio are consistent.

(1) Near the CS vent, we try to give an estimate of the Cl/S mass ratio. At 15 m from the vent we measured 3 ppm of SO_2 and 8 ppm of H_2S with

LIII. We assume that the HCl/SO_2 molar ratio is the same for the three emission points of the vent. With the OP-FTIR we measured a HCl/SO_2 molar ratio of 40 ± 7 (Table 3) from the CSS emission point. Then we calculated a Cl/S molar ratio $\frac{40[SO_2]}{[SO_2]+[H_2S]} = 11 \pm 2$. This corresponds to a Cl/S mass ratio of 9.4 ± 1.7.

(2) At 140 m from the CS vent, the HCl/SO_2 molar ratio is 10 ± 2. This value remained the same on different days. From interpolation of the curves of Fig. 6 we deduce a SO_2/H_2S ratio near 2 at 140 m from the vent and calculate a Cl/S molar ratio $\frac{10[SO_2]}{[SO_2]+[H_2S]} = 3.5 \pm 0.7$. This corresponds to a Cl/S mass ratio of 2.8 ± 0.6.

Due to the higher solubility of HCl compared to those of SO_2 and H_2S, more HCl will partition into liquid droplets of the plume. Preferential scavenging of HCl in and near the vent will lead further to smaller Cl/S ratios. The lower value obtained for Cl/S at 140 m compared to 15 m from the vent is also in agreement with the different rates of HCl and SO_2 depletion due to chemical reactions inside the plume and plume–atmosphere interactions discussed above.

The Cl/S mass ratios we measured in the CS plume at La Soufrière are high compared to other volcanoes (Symonds et al., 1994, 1996; Mori et al., 1995; Hammouya et al., 1998; Oppenheimer et al., 1998a,b,c).

High HCl/SO_2 are generally associated with eruptive and post-eruptive phases (Symonds et al., 1994): during the magma degassing, HCl concentration generally increases whereas SO_2 decreases since the low soluble SO_2 exsolves prior from the magma. HCl/SO_2 is generally lower than 1 in a pre-eruptive phase and increases when the magma moves toward the surface and degasses. Compared to other magma types, andesite–dacite magma of subduction zone are generally associated with volcanic gases rich in water vapor and chlorine. Cl/S is higher (from 0.03 to 10) in samples from convergent-plate volcanoes than in samples from divergent-plate and hot-spot volcanoes (0.006 to 0.05; Symonds et al., 1994).

4.3. Origin of present degassing at La Soufrière

Silicic magmas erupt in a wide range of styles and there is no simple general model for andesite volcano degassing (Symonds et al., 1994; Sparks, 1997; Webster et al., 1999; Villemant and Boudon, 1999; Francis et al., 2000; Edmonds et al., 2001; Straub and Layne, 2003; Villemant et al., 2003a; Manning, 2004; Wallace, 2005). Dissolved volatiles species may reach

saturation in a magma in response to pressure decrease (magma ascent) or to variation of the melt composition due to crystallization. When saturation is reached, the fluid phase may exsolve. Composition and fluxes of emitted gases can be influenced by various processes such as deep versus shallow exsolution, second boiling, infiltration of sea or meteoric water, or fluid–rock interactions.

4.3.1. Comparison to degassing processes associated to four selected volcanoes

To better understand the origin of the present degassing at La Soufrière, we report in this section conclusions on degassing processes in four selected volcanoes two of which presenting high Cl/S ratios. These studies generally combine several data types: remote or direct measurements of volcanic gas compositions and volatile contents of melt (glass) inclusions representative of non-erupted magma.

4.3.1.1. Soufrière Hills, Montserrat. We paid special attention to gas studies and OP-FTIR results obtained on Soufrière Hills volcano, Montserrat (Chiodini et al., 1996; Hammouya et al., 1998; Oppenheimer et al., 1998a,c,d; Edmonds et al., 2001, 2002) since this volcano is located in the same subduction area as La Soufrière. Prior to 1995, Soufrière Hills maintained an intense hydrothermal activity but there was no manifestation inside the summit crater before July–August 1995. Chiodoni et al. (1996) and Hammouya et al. (1998) study the gas discharged from the four main fumaroles around Soufrière Hills before 1995 eruption. The gas temperatures were low, below 100 °C. Chemical compositions of the fumarolic vapors show no HCl, HF and SO_2, which suggests their hydrothermal origin. It is only in February 1996 that Hammouya et al. (1998) have detected HCl (16.7%) and SO_2 (3.8%) in high temperature (720 °C) gas samples collected on an incandescent vent of the lava dome. In the literature, we found no reference to these dangerous measurements. The sampling was carried out on a lava dome that had been growing since September 1995 and undergoing periodic landslides. They derived a HCl/S_{tot} molecular ratio of about 4.4. This high ratio was confirmed by Oppenheimer et al. (1998c) by OP-FTIR measurements in July–August 1996 (HCl/$SO_2 \geq 10$). Hammouya et al. (1998) underlined that high Cl/S is a rare feature only encountered in a few arc volcanoes in post eruptive phase as Showa–Shinzan, Japan (Symonds et al., 1996). Changes in HCl/SO_2 ratios rapidly occur in the plume and they have been used to predict the eruption evolution at Soufrière Hills.

Edmonds et al. (2001) show that the chlorine is derived from the andesitic magma and degasses during the magma uprise. Smaller chlorine contents of the matrix glasses (100–2400 ppm) compared to melt inclusions (3500–4500 ppm) result from fractional crystallization combined with the partitioning of Cl into a water-rich fluid phase (with a fluid–melt partition coefficient very high, ~50). Sulfur source was not andesite but a mafic magma that intruded into the andesite magma chamber to trigger eruption. This mafic intrusion recharged the sulfur contents of the shallow volcanic system. They concluded that high SO_2 and HCl fluxes with HCl/SO_2 molar ratio of 1 to 12 are associated with effusive dome-building episodes (in an open degassing regime).

4.3.1.2. Showa Shinzan dome, Usu, Japan. Symonds et al. (1996) studied an increasing Cl/S (from 1 to 6) due to a sudden increase of HCl in high temperature (>500 °C) gas emissions from Showa Shinzan dome (Usu, Japan), between 1954 and 1964. This dome formed several years before, during the 1943–1945 eruption of Usu volcano (Japan). Since this period the dome kept degassing. Symonds et al. (1996) explained the Cl/S increase as the result of a 'second boiling' of the magma in which Cl was preferentially exsolved from a residual melt already depleted in S. Volatiles exsolution is typically categorized as either first or second boiling or some combination of both (Symonds et al., 1996; Webster et al., 1999). The first boiling corresponds to a degassing related to the magma ascent through shallow crustal depths, the degassing being due to the solubility reduction of the volatiles with decreasing pressure. This effect is important for H_2O and CO_2 that present high degassing in first boiling, but is negligible for chlorine. Second boiling results from increasing abundance of volatiles in residual melt driven by a reduction in temperature and/or enhanced crystallization. Crystallization causes water exsolution, which causes loss of chlorine from the melt (Webster et al., 1999; Villemant and Boudon, 1998, 1999; Edmonds et al., 2001; Webster and De Vivo, 2002; Villemant et al., 2003a,b).

4.3.1.3. Redoubt, Alaska. In the 1989–1990 eruption, this volcano presented extremely high SO_2/HCl ratio despite relatively high Cl concentrations in both phenocryst and matrix glasses. Gerlach et al. (1994) concluded that the very low measured HCl concentrations in the plume were due to selective scavenging by water vapor. Scrubbing can efficiently trap volcanic gases and mask magmatic degassing (Symonds et al., 2001). They

also show, through melt inclusion analyses, evidence of pre-eruptive accumulation of magmatic vapour at 6–10 km depth.

4.3.1.4. Etna, Sicily. Allard et al. (2005) provided a detailed record of the chemical evolution of magmatic gas during and after a powerful lava fountain on Mount Etna (Sicily). Etnean gases arise from exceptionally water-rich basalts. The CO_2/S and S/Cl ratio evolved from very high value during lava fountain to 2 to 4 times lower values after the paroxysmal phase. They argued than syn-eruptive bulk magma degassing is improbable and concluded that lava fountains were most probably driven by the separate ascent of a gas layer previously accumulated at moderate depth, rich in S and CO_2. CO_2 exsolves earlier than S, and S prior to Cl. Low S/Cl is associated to degassing of the cooling magma and earlier exhaustion of S relative to Cl.

4.3.2. Tentative explanation of La Soufrière degassing

These examples lead us to a tentative explanation of the new degassing at the summit vents since 1992 and the sudden appearance of HCl in 1998 at La Soufrière.

The behavior at Soufrière Hills with a deep versus shallow gas exsolution associated with magma uprising movements seems unlikely at La Soufrière of Guadeloupe since we are out of eruption, with no large scale deformation and no seismicity at depth till now.

Even a slow dome cooling model is not adapted to describe La Soufrière behavior, as Usu La Soufrière should undergo a secondary degassing since 1992, possibly induced by a notable modification in magma composition due to crystallization. Residual volatile species dissolved in the magma may have reached saturation in response to variation of the melt composition, and exsolve. Then, Cl-rich gases at La Soufrière is due to the degassing of a magma depleted in S. During the 1976–1977 phreatic eruption, higher H_2S and SO_2 emissions had been observed and isotopic analyses suggested the occurrence of magmatic gas emissions. Using the results of Hirn and Michel (1979) who studied the seismicity during this crisis, Feuillard et al. (1983) located the origin of those magmatic gases at the top of the magma chamber, near 6 km at depth (Vincent et al., 1979). They interpreted the 1976–1977 crisis as a 'still-born' magmatic eruption. Then, Vincent (1994) suggested a second boiling as a possible evolution for La Soufrière. The second boiling hypothesis implies the presence of large volumes of gas under pressure in the magmatic chamber. This would constitute a great hazard. This trapped gas phase may

contain much HCl since a great part of SO_2 (and H_2S) has already left the magma chamber.

Etna and Redoubt volcanoes also show evidence that gases can dissolve from an un-erupted magma (non-syn-eruptive degassing) and form a separate fluid in magma chamber which could be emitted during co-eruptive or fumaroles (steady degassing) activity. Modifications inside La Soufrière hydrothermal system should make easier the uprise of these gases towards the surface. This second hypothesis does not imply notable modification in the magma degassing state. At La Soufrière, an increase of fumarolic and seismic (Fig. 7) activity began in 1992. Unpublished data on isotopic measurements on Cl in La Soufrière condensates by N. Jendrzejewski (pers. comm.) suggest the magmatic origin of the South Crater gas emissions. Villemant et al. (2003b) considered data on long-term chemical monitoring of fumaroles at La Soufrière and hydrothermal springs associated with the volcanic structure, obtained using direct sampling methods over the 1970–1992 period. They analyzed them in term of periodic injection of HCl- and HBr-rich gases from a degassing shallow magma body. Temporal study of four hot springs shows an increasing tendency in their $\delta^{37}Cl$ (Jendrzejewski and Agrinier, pers. comm.) and suggests an increasing influence of volcanic gas components in the system.

An increase of the stress in the summit area may even have opened small fractures along the central axis of the volcanic system and then facilitated the uprising of volatiles trapped in the magma chamber. Self Potential measurements at La Soufrière in 1992 and 1998 (Zlotnicki et al., 1994) indicate a progressive sealing of the hydrothermal system in its peripheral zones and a migration of fluid transfer area toward the central part of the volcano, in agreement with the preferential degassing observed at the summit since 1992. Moreover, this sealing may limit interactions between the released magmatic gases and the hydrothermal fluids, and scavenging effects.

Other origins for La Soufrière Cl-rich gases are also possible like a high original abundance of chlorine relative to sulfur in La Soufrière magma. Seawater trapped in subducted oceanic crust provides a source of water and chlorine enrichment in parent magma for convergent-plate volcanoes which present high pre-eruptive H_2O and Cl contents (Allard, 1983; Symonds et al., 1994; Webster et al., 1999; Manning, 2004). Chlorine contents of dacitic to rhyolitic melt inclusions in arc volcanic rocks vary from 900 to 2200 ppm (Wallace, 2005). Very high values in volcanic products from Somma–Vesuvius (up to 8000 ppm) suggest that, Cl-enriched mafic magmas can be saturated with respect
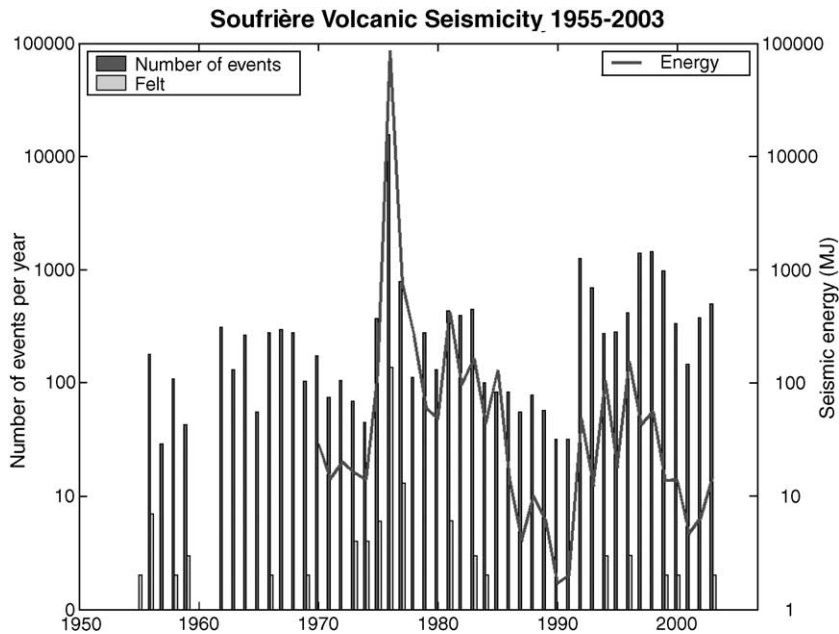
Fig. 7. La Soufrière volcanic seismicity from 1955 to 2003.

to an hydrosaline liquid (Cl-rich aqueous brine phase) at shallow crustal conditions (Signorelli and Carroll, 2000; Webster and De Vivo, 2002; Webster, 2004).

If La Soufrière magma is particularly rich in Cl, it may be saturated with a Cl-rich aqueous phase. Estimation on pre-eruptive Cl contents from La Soufrière volcanic clasts are necessary to conclude. Presently, no published data are available. However initial melt concentrations estimated at Mount Pelée, Martinique, for the 650 y. B.P. eruption (P1) (H_2O 5.5% and Cl~2100 ppm) (Villemant and Boudon, 1999) and at Soufrière Hills (H_2O 4–5% and Cl~3400 ppm) (Devine et al., 1998; Edmonds et al., 2001) suggest relatively Cl-rich magma in the Lesser Antilles arc. These two volcanoes are located in the same subduction zone as La Soufrière. Villemant and Boudon (1999) pointed that such Cl contents are close to the upper Cl solubility limit at magma storage conditions (200 MPa and 900 °C) in H_2O-saturated aluminious rhyolitic melts (≈ 2500 ppm). They calculated Cl partition coefficient between aqueous fluids and rhyolitic melts and show that stronger values correspond to an open system degassing model with simultaneous melt crystallization.

An other interpretation of La Soufrière emissions should be an enhanced vaporization of Cl-rich aquifers since 1998 due to the gradual sealing of the system and enhanced confinement of the gas flow through the main active vent (CS). The appearance of HCl was too sudden to support such hypothesis, moreover no enrichment in HCl has been observed in the sources near the dome.

5. Conclusion

This study presents the successful measurement of the plume composition of La Soufrière of Guadeloupe, despite the difficult meteorological conditions, using active remote sensing OP-FTIR measurements. These first OP-FTIR measurements of La Soufrière out of eruption confirm the presence of volcanic HCl gas in relatively high concentrations in the plume: 60 to 300 ppmv m or a concentration of 2.4 to 12 ppmv with an estimated plume width of 25 m. They confirm the high acidity of the South Crater plume estimated from pH measurements. This pH is presently lower than 1, which means 2000 ppm of HCl gas at the vent. The fast dissolution in water droplets of the plume at low temperature reduces the gaseous HCl measured by OP-FTIR. Combined Lancom III analyses showed that the Cl/S_{tot} mass ratios are high: from 9.4 ± 1.7 at 15 m from the vent to 2.8 ± 0.6 at 140 m. Comparison with other volcanoes located in subduction zones and presenting high Cl/S ratios allows us to propose different hypothesis on the origin and acidity of La Soufrière present degassing. A second boiling of a Cl-rich magma at shallow depth and enhanced transfer of volcanic gases versus the surface are consistent with the data presented in this study. The enrichment in HCl of the emitted gas since 1998 should correspond to a later exsolution of HCl compared to SO_2 firstly emitted from magma. An original Cl-rich magma can also contribute to the measured high Cl contents. The seismic reacti-

vation in 1992 may have opened fractures and facilitated the uprising of gases to the summit.

Presently, detailed isotopic analyses of La Soufrière gases and chemical analyses of melt inclusions are necessary to validate or not the proposed interpretative models.

The presence of HCl and its possible magmatic origin imply volcanic hazards. More OP-FTIR measurements at regular intervals should be carried out in order to observe an evolution of the plumes and particularly of HCl concentrations at La Soufrière. Since magmatic CO_2 is less sensitive to H_2O vapor phase, hydrothermal system and air interactions, CO_2 may be a useful indicator of magma degassing (Symonds et al., 1994; Francis et al., 2000). Special effort will be done in the future to also monitor magmatic CO_2 with OP-FTIR. Such data could be compared to other parameters, deformation and seismicity, to better understand the behavior and predict possible future evolution of this volcano.

Acknowledgements

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