

# **Geophysical Research Letters**

# **RESEARCH LETTER**

#### **Kev Points:**

- H<sub>2</sub>S dissolution and oxidation is inefficient in pH 2-3 lakes
- Sulfur degassing through pH 2-3 lakes is a kinetically driven process SO<sub>2</sub> degassed from pH 2-3 lakes
- originates from H<sub>2</sub>S oxidation with sulfites as transient species

#### **Supporting Information:**

- Data S1
- Table S1

#### Correspondence to:

N. Hasselle, nathalie.hasselle@unipa.it

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# Sulfur Degassing From Steam-Heated Crater Lakes: El Chichón (Chiapas, Mexico) and Víti (Iceland)

N. Hasselle<sup>1</sup> (D, D. Rouwet<sup>2</sup>, A. Aiuppa<sup>1,3</sup> (D, M. P. Jácome-Paz<sup>4</sup>, M. Pfeffer<sup>5</sup> (D, Y. Taran<sup>4</sup>, R. Campion<sup>4</sup>, M. Bitetto<sup>1</sup>, G. Giudice<sup>3</sup> (D), and B. Bergsson<sup>5</sup>

<sup>1</sup>Dipartimento DiSTeM, Università di Palermo, Palermo, Italy, <sup>2</sup>Istituto Nazionale di Geofisica e Vulcanologia, Bologna, Italy, <sup>3</sup>Istituto Nazionale di Geofisica e Vulcanologia, Palermo, Italy, <sup>4</sup>Instituto de Geofísica, Universidad Nacional Autónoma de México, Mexico City, Mexico, <sup>5</sup>Icelandic Meteorological Office, Reykjavik, Iceland

Abstract The composition of the gases released by El Chichón (Chiapas, Mexico) and Víti (Askja volcano, Iceland) volcanic lakes is examined by Multi-GAS for the first time. Our results demonstrate that H<sub>2</sub>S and  $SO_2$  are degassed by these pH 2–3 lakes. We find higher  $CO_2/H_2S$  and  $H_2/H_2S$  ratios in the lakes' emissions (31-5,685 and 0.6-35, respectively) than in the fumarolic gases feeding the lakes (13-33 and 0.08-0.5, respectively), evidencing that only a fraction (0.2-5.4% at El Chichón) of the H<sub>2</sub>S<sub>(q)</sub> contributed by the subaquatic fumaroles ultimately reaches the atmosphere. At El Chichón, we estimate a H<sub>2</sub>S output from the crater lake of 0.02–0.06 t/day. Curiously, SO<sub>2</sub> is also detected at trace levels in the gases released from both lakes (0.003-0.3 ppmv). We propose that H<sub>2</sub>S supplied into the lakes initiates a series of complex oxidation reactions, having sulfite as an intermediate product, and ultimately leading to SO<sub>2</sub> production and degassing.

Plain Language Summary Volcanic lakes are the site of some of the most unpredictable, and therefore dangerous, volcanic eruptions in nature. Their activity is driven by a feeding volcanic gas phase supplied by the underlying hydrothermal/magmatic system. These volatile species, entering the lake bottom, are absorbed into lake water at different rates/degrees depending on their water solubilities and the lake physical and chemical characteristics. Hyperacidic crater lakes (pH <1) are degassing SO<sub>2</sub>, a gas that was earlier believed to be totally dissolved into the water. In this study, we investigate for the first time the presence of reactive S gases (SO<sub>2</sub> and H<sub>2</sub>S) in the plumes of less acidic (pH 2-3) lakes El Chichón (Mexico) and Víti (Iceland). Our results demonstrate that H<sub>2</sub>S, coming from the sublimnic hydrothermal systems is only partially dissolved and oxidized by the lake water. In addition, we discover trace amount of SO<sub>2</sub> coming off both lakes. We propose that  $SO_2$  is produced into the lake by  $H_2S$  oxidation, with dissolved sulfite as an intermediate product. Our results thus open new piece of knowledge to our understanding and monitoring the activity of restless volcanic lakes.

# 1. Introduction

The volcanic lakes filling the craters of several dormant and active volcanoes worldwide (Rouwet et al., 2015) are known to act as traps of water-soluble volcanic volatiles escaping from the volcano's edifice (Rouwet et al., 2014). Due to their high reactivity to aqueous solutions, sulfur species originating from deeper hydrothermal/magmatic sources are traditionally thought to be efficiently scrubbed by water bodies, including groundwaters, hydrothermal aquifers, and volcanic lakes (Symonds et al., 2001; Varekamp, 2015; Varekamp et al., 2000). Recent Multi-GAS compositional measurements in the plumes of hyperacidic crater lakes (de Moor et al., 2016; Gunawan et al., 2016; Shinohara et al., 2015; Tamburello et al., 2015) have shown that SO<sub>2</sub> escapes through lake-water surfaces during pH < 1 gas-water interactions. HCl, another acidic gas species generally considered reactive in aqueous solutions, was detected in emissions from hyperacid springs (e.g., Kalacheva et al., 2016). Recently, Capaccioni et al. (2017) and Rodríguez et al. (2017) experimentally demonstrated that HCl is increasingly released from a "lab-lake" when pH drops below -0.2.

In this study, we test the hypothesis of whether or not sulfur species are also actively degassed from two less acidic (pH ~2-3) crater lakes. Our test sites are the volcanic lakes hosted in the volcanic craters of El Chichón, Chiapas, Mexico (Figure S1; Mazot et al., 2011; Rouwet et al., 2008; Taran & Rouwet, 2008) and Askja (Víti lake, Iceland; Figure S1). El Chichón (17°22'N, 93°14'W) is a trachy-andesitic dome complex located in the northwest of Chiapas, Mexico, and was poorly known until its Plinian eruption in March-April 1982 which formed a 1.1-km-wide circular crater (Sigurdsson et al., 1984; Varekamp et al., 1984). Soon after the eruption, a hot

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(T = 52-58 °C) and highly acidic (pH = 0.56) lake appeared on the crater floor (Casadevall et al., 1984) that has changed (in 2016, T~30 °C and pH~2.75) but persisted since. The lake and hydrothermal manifestations in the crater have been extensively studied (Armienta et al., 2000; Jácome Paz et al., 2016; Mazot et al., 2011; Mazot & Taran, 2009; Peiffer et al., 2015; Rouwet et al., 2004, 2008, 2009; Taran et al., 1998; Taran & Peiffer, 2009; Taran & Rouwet, 2008). Víti crater lake (65°02′N, 16°43′W), situated in east-central Iceland, was formed by a phreatic explosion inside the Askja volcano caldera, following its 1875 plinian eruption (Carey et al., 2009; Sigvaldason, 1979). Few low-temperature fumaroles are located along the eastern and southern shores of the lake. Both lakes are large (in 2016, ~1.54 × 10<sup>5</sup> m<sup>2</sup> for El Chichón and ~7.8 × 10<sup>3</sup> m<sup>2</sup> for Víti) steam-heated pools where dissolved oxidized sulfur compounds originate mainly from oxidation of H<sub>2</sub>S sourced at the lake bottom (maximum depth ~4.5 m at El Chichón and ~60 m at Víti) by the underlying hydrothermal systems.

Here we report on Multi-GAS measurements made at the air-lake interface at both sites. We show that  $H_2S$  and trace  $SO_2$  are effectively escaping these pH~2–3 lakes. By comparing the emissions from the lakes with the composition of emissions from subaerial fumaroles (treated as a proxy for the gas feeding to the lakes), we attempt at characterizing the chemical modifications driven by gas-lake water interactions, and the processes responsible for gas leakage through the lakes.

# 2. Methodology

We investigate the composition of gases emitted by (i) subaerial fumaroles around the lakes (*fumarole gas*), (ii) hot pools on the lake shore (only at El Chichón; *pool gas*), and (iii) gas at the air-lake interface (*lake gas*), sourced by surface degassing by either diffusion (no bubbling) or advection (bubbling lake degassing). Gas compositions were measured in situ by Multi-GAS (Multicomponent Gas Analyzer System; Aiuppa, Federico, et al., 2005; Shinohara, 2005). We used a compact sensor unit containing a nondispersive infrared spectrometer (for CO<sub>2</sub>; range = 0–3000 ppm), three electrochemical gas sensors for H<sub>2</sub>S (range = 0–100 ppm), SO<sub>2</sub> (range = 0–200 ppm), and H<sub>2</sub> (range = 0–200 ppm) and a relative humidity sensor (range = 0–100%) for indirectly measuring H<sub>2</sub>O. This instrument has been used previously to measure composition of gas released by fumarolic vents and open-conduit volcanoes (e.g., Aiuppa et al., 2009, 2011, 2012, 2014), by hyperacidic crater lakes (e.g., Yudamari, Shinohara et al., 2015; Copahue, Tamburello et al., 2015; Poás, de Moor et al., 2016; Kawah Ijen, Gunawan et al., 2016), and at the less acidic Boiling Lake, Dominica (pH 4–6; Di Napoli et al., 2014). This is the first reported use of the Multi-GAS to measure weakly sulfur-degassing crater lakes without vigorous emissions.

Continuous measurements were made of lake gases, close to the lake surface, from a slowly moving boat. An anticipated challenge when measuring gases coming weakly from lakes are low concentrations, close to the sensor detection limits. Three sampling configurations were tested in order to measure the highest lake gas concentrations and minimize their atmospheric dilution: (i) measurements about 30–40 cm above the lake surface at the more vigorously degassing El Chichón lake; (ii) measurements about 10 cm above the surface, with a 20-cm-diameter overturned funnel attached to the inlet; and (iii) with the attached funnel kept floating on the surface of the lake at the more weakly degassing Viti lake. This latter configuration allows for the detection of very low SO<sub>2</sub> concentrations (<<1 ppmv; see Figure S2), but is complicated by the rapid saturation of the CO<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub> sensors. Moreover, as the relative humidity increases inside the funnel with time, functioning of electrochemical sensors (SO<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>) will be affected.

At El Chichón, gas measurements were made on 3 March 2016, with good meteorological conditions (no rain and low wind). Fumarole gas measurements were completed on 4 March 2016, after 3 hr of rain. At Víti, measurements were made on 16–17 August 2016. Due to wind, it was impossible to visually distinguish areas with bubbles on the lake, except close to the lake shore. Surface temperature and pH were measured at both lakes, and lake water samples were collected for later analysis for major cations and anions using standard ion chromatography methods (at IGF-UNAM and INGV-Palermo; see Table S1).

## 3. Results

#### 3.1. Gas Composition and SO<sub>2</sub> Detection

The pH (2.76 ± 0.37), temperature (21.8 ± 1.16 °C), and chemical composition of Víti lake were homogenous (Table S1). El Chichón lake was more heterogeneous with a mean pH of 2.75 ± 0.02 and temperature of  $30.1 \pm 1$  °C (chemical composition at the lake center is detailed in Table S1).





**Figure 1.** Examples of  $CO_2$  versus  $H_2S$  scatterplots at (a and b) El Chichón and (c) Víti and of  $SO_2$  versus  $H_2S$  scatterplots at (d) both volcanoes. Ratios values corresponding to the regression lines are written in the plots with their errors in parenthesis. Plot (c) shows the fumarolic composition ( $CO_2/H_2S$  ratios between these of offshore fumaroles, located several meters from the lake shore, and lake fumaroles, situated at 30 cm from the shore) of gases coming off strong bubbling in shallow water (20–30 cm) at Víti (called lake-big bubbles). In the paper, those ratios are therefore assimilated to fumaroles. Plot (d) illustrates the lower  $SO_2$  concentrations measured at Víti compared to El Chichón but also the increase of the  $SO_2/H_2S$  ratio as followed: Fumaroles < hot pools < bubbling lake gas < diffuse degassing.

Fumarole gases, pool gases, and lake gases at both volcanoes were dominated by  $H_2O$  and  $CO_2$  (10–1000s of ppmv).  $H_2S$  (up to ~7 ppmv at El Chichón and at ~100 ppmv at Víti) and  $H_2$  (up to 50 and 70 ppmv at El Chichón and Víti, respectively) were unambiguously measured in the lake gases at both lakes (Figures 1a–1c). Small amounts of SO<sub>2</sub> in the lake gases of both volcanoes (<0.3 and <0.003 ppmv for El Chichón and Víti, respectively; see Figure 1d) were also measured.

We caution that, given the low concentrations measured, well below the typical calibration range of SO<sub>2</sub> sensor (1–100 ppmv), our SO<sub>2</sub> ratios should not be viewed as truly quantitative for this gas. However, our SO<sub>2</sub> concentrations exhibit a positive correlation ( $R^2 > 0.6$ ) with H<sub>2</sub>S (Figure 1d), CO<sub>2</sub>, and H<sub>2</sub>O (Figure S2b), strongly suggesting that the SO<sub>2</sub> peaks are real, and not artifacts due to the sensor's noise. In addition, based on laboratory tests using 50–100-ppmv H<sub>2</sub>S standard gases, we did not stimulate false SO<sub>2</sub> signals with H<sub>2</sub>S gas (cross-sensitivity to H<sub>2</sub>S of the SO<sub>2</sub> sensor is 0 according to our laboratory tests). As such, our El Chichón and Víti results should be intended as reflecting that SO<sub>2</sub> is actually present in the lake gases at sub ppmv levels.

At El Chichón, Taran et al. (1998) and Mazot et al. (2011) measured low amounts of  $SO_2$ , and interpreted its presence as not being magmatic, but rather due to secondary processes (i.e., saline water droplets in the collecting bottles). At Víti, very low  $SO_2$  amounts were measured in fumarole gases (93 °C) around the lake perimeter and in advected lake gases above very shallow subaquatic fumaroles (96 °C; Figure 1d). The detection of  $SO_2$  in lake and pool gases is unusual. No  $SO_2$  has previously been measured in gases emitted



**Figure 2.** (a)  $SO_2/H_2S$  versus  $CO_2/H_2S$  ratios and (b)  $H_2/H_2S$  versus  $CO_2/H_2S$  ratios measured in El Chichón and Víti plumes. Data references are listed in Table 1. The ratios symbolized by empty circles with a cross inside correspond to  $H_2$  or  $CO_2$  versus total sulfur instead of  $H_2S$ . At both volcances, red arrows show the scrubbing effect of lake waters on gas ratios. In addition, in plot (a), the transition from more magmatic (in 1983) to hydrothermal (since at least 2008) fumarolic gas composition is shown with decreasing  $SO_2/H_2S$  and  $CO_2/H_2S$  ratios through time at El Chichón (black arrow). Since 2008, the fumarolic  $SO_2/H_2S$  (10<sup>-2</sup> to 10<sup>-3</sup>),  $CO_2/H_2S$  (13-33), and  $H_2/H_2S$  (0.08–0.7) ratios are stable.

by pH 2–3 lakes as it has been believed to be completely dissolved at such pH (Symonds et al., 2001). Hence, we suggest that it may be produced in the lake by a secondary oxidative process.

### 3.2. Gas Ratios

Figure 2 shows scatterplots comparing fumarole gases and lake gases in terms of volatile ratios  $SO_2/H_2S$  versus  $CO_2/H_2S$  and  $H_2/H_2S$  versus  $CO_2/H_2S$ . El Chichón and Víti gas manifestations exhibit similar trends: the lowest values for all ratios are measured in fumarole gases, and the highest in the lake gases. Pool gases exhibit intermediate values (Figures 2a and 2b).

At El Chichón, the time series for SO<sub>2</sub>/H<sub>2</sub>S and CO<sub>2</sub>/H<sub>2</sub>S ratios from fumarole gases (Figure 2a) are available dating back to the 1982 eruption (Casadevall et al., 1984; CCVG Newsletter, 2010; Mazot et al., 2011; Taran et al., 1998; Tassi et al., 2003). These clearly show a trend from more magmatic compositions in 1983 (SO<sub>2</sub>/H<sub>2</sub>S = 7, CO<sub>2</sub>/H<sub>2</sub>S = 291) to more hydrothermal compositions soon after (Taran et al., 1998; Tassi et al., 2003). Since 2008, fumarolic CO<sub>2</sub>/H<sub>2</sub>S ratios have clustered at values (13–33) representative of hydrothermal conditions, whereas SO<sub>2</sub>/H<sub>2</sub>S ratios have shown larger spread (10<sup>-2</sup> to 10<sup>-3</sup>; Figure 2a). This H<sub>2</sub>S-rich hydrothermal gas is assumed to be a proxy for the composition of the subaquatic fumaroles feeding the lake today.

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5as Ratios and R <sub>H</sub> (Giggenbach,	, 1987) Measured With the Mull	tiGAS (This Study) or	by Direct Gas Samplin	ig (Literature Data) i	n Gas Plumes at El Ch	iichón and Víti V	olcanoes
Plume type	SO <sub>2</sub> /H <sub>2</sub> S	CO <sub>2</sub> /H <sub>2</sub> S	H <sub>2</sub> /H <sub>2</sub> S	H <sub>2</sub> 0/C0 <sub>2</sub>	CO <sub>2</sub> /H <sub>2</sub>	R <sub>H</sub>	Reference
Lake—diffuse degassing	$4.0-5.3 \times 10^{-1}$ $(4.7 \times 10^{-1})$	615-5,685 (2,042)	0.8-14.5 (5.3)	0.6–32 (12)	167–1,429 (333)	-3.2 to -2.7	This study
Lake—bubbling gas	$3-15 \times 10^{-2} \ (7 \times 10^{-2})$	1,330-5,090 (2,637)	3.4–35 (14.8)	0.5-4.4 (2.2)	71–556 (147)	-3.2 to -1.6	This study
Hot pools	$10-24 \times 10^{-3}$ ( $16 \times 10^{-3}$ )	100–393 (256)	0.2–3.3 (1.6)	0.02-3.55 (0.97)	91–500 (200)	-3.2 to $-0.7$	This study
Fumaroles	$1-7 \times 10^{-3} (3 \times 10^{-3})$	13–33 (23)	0.08-0.5 (0.25)	0.03-1.8 (0.51)	59-167 (100)	-2.4 to -0.4	This study
Fumaroles (1983–2008)	$1-70,000  imes 10^{-4}$	15–291	0.1–5.7	0.2–142, 2.5–84.3 <sup>b</sup>	17–333	-4.2 to -1.1	Casadevall et al. (1984),
				(between 1996			Taran et al. (1998), Tassi
				and 2005)			et al. (2003), Mazot et al.
							(2011), and CCVG
							Newsletter (2010)
Strongly bubbling gas (2008)	$3 \times 10^{-2}$	44-390	0.2–2.5	0.08-0.9	25–333	-2.3 to -1.31	CCVG Newsletter (2010)
Lake—diffuse degassing	$3-10 \times 10^{-4}$	44-163 (101)	0.6-4.2 (1.7)	n/a	20-167 (50)	n/a	This study
Lake—bubbling gas	$10-16 \times 10^{-4}$	31–175 (61)	0.14–2.7 (0.7)	0.05-0.3 (0.17)	33–250 (100)	-1.8 to -0.6	This study
Fumaroles <sup>a</sup>	$28-34 \times 10^{-5}$ ( $31 \times 10^{-5}$ )	15–27 (22)	0.23–0.49 (0.39)	5 (±1.3 <sup>c</sup> )	48-67 (56)	-2.5	This study
Fumaroles (2014–2017)	$4-8 \times 10^{-3} (6 \times 10^{-3})$	11.3–64.2 (29.3)	0.0045-0.036 (0.02)	1–23 (7)	1,149–2,632 (1,471)	-4.1 to -3.3	This study
values in parenthesis are the r s the offshore fumaroles but a and in 2008 the water vapor	means. Also the shallow subaquatic fui was mostly condensed in the	maroles close to the sampling fumarolic	shore (see Figures 10 gas. Therefore, they o	t and 1d for explane cannot be used to c	ation). <sup>b</sup> The fumarol ompare to the preser	les before 1996 nt H <sub>2</sub> O/CO <sub>2</sub> rati	have higher temperature os. <sup>C</sup> Error.
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$1-7 \times 10^{-3}$ ( $3 \times 10^{-3}$ ) $13-33$ ( $233$ ) $0.08-0.5$ ( $0.253$ )         Strongly bubbling gas ( $2008$ ) $3 \times 10^{-3}$ $13-32$ ( $231$ ) $0.1-5.7$ Strongly bubbling gas ( $2008$ ) $3 \times 10^{-2}$ $44-390$ $0.2-2.5$ Lake—bubbling gas ( $2008$ ) $3 \times 10^{-2}$ $44-390$ $0.2-2.5$ Strongly bubbling gas ( $2008$ ) $3 \times 10^{-2}$ $44-390$ $0.1-2.7$ ( $0.7$ )         Lake—bubbling gas ( $2008$ ) $3 \times 10^{-5}$ $31-775$ (	Sar Ratios and R <sub>H</sub> (Giggenbach, 1987) Measured With the MultiGAS (This Study) or by Direct Gas Sampling (Literature Data) i           Flume type         SO <sub>2</sub> /H <sub>2</sub> S         CO <sub>2</sub> /H <sub>2</sub> S         H <sub>2</sub> /H <sub>2</sub> S         H <sub>2</sub> O/CO <sub>2</sub> Plume type         SO <sub>2</sub> /H <sub>2</sub> S         CO <sub>2</sub> /H <sub>2</sub> S         0.6-32 (12)         0.6-32 (12)           Lake—diffuse degassing $4.0-5.3 \times 10^{-1} (4.7 \times 10^{-1})$ 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El Classe degassing $4.0-5.3 \times 10^{-1}(4.7 \times 10^{-1})$ $615-5,685$ (2,042) $0.8-14.5$ (5.3) $0.6-32$ (12) $167-1,429$ (333) Lake—bubbling gas $3-15 \times 10^{-2}(7 \times 10^{-2})$ $1,330-5,090$ (2,637) $3.4-35$ (1.48) $0.5-44$ (2.2) $71-556$ (147) Hot pools $1-7 \times 10^{-3}$ ( $5 \times 10^{-3}$ ) $15-291$ $0.0-331$ (1.6) $0.02-335$ ( $0.97$ ) $91-500$ ( $000$ ) Fumaroles (1983-2008) $1-70,000 \times 10^{-4}$ $15-291$ $0.1-5.7$ $0.2-44.2$ ( $2.2$ ) $71-556$ ( $147$ ) $1-7333$ ( $150$ ) $0.3-18$ ( $0.51$ ) $91-500$ ( $000$ ) Fumaroles (1983-2008) $1-77,000 \times 10^{-4}$ $15-291$ $0.1-5.7$ $0.2-44.2$ ( $2.2$ ) $71-556$ ( $147$ ) $1-7333$ ( $160$ ) $0.2-35$ ( $0.97$ ) $91-500$ ( $000$ ) Fumaroles (1983-2008) $3 \times 10^{-3}$ ( $15-2683$ ( $14,8$ ) $0.1-5.7$ $0.2-44.2$ ( $17$ ) $0.2-44.2$ ( $17$ ) $17-333$ ( $166$ ( $100$ ) $1-72$ ( $170$ ) $1-72$ ( $170$ ) $0.2-44.2$ ( $170$ ) $0.2-44.2$ ( $170$ ) $0.2-44.2$ ( $170$ ) $0.2-44.2$ ( $170$ ) $0.2-44.2$ ( $170$ ) $0.2-44.2$ ( $120$ ) $0.2-167$ ( $000$ ) $1-24$ ( $140-400$ ) $1-24$ ( $11-26$ ) $1-2-77$ ( $11-6$ ( $11-7$ $0.1-5.7$ ( $11-6$ ( $11-26$ ) $1-2-77$ ( $11-7$ $0.1-5.7$ $0.2-44.2$ ( $120$ ) $0.2-44.2$ ( $12$	Gas Ratios and $R_{H}$ (Giggenbach, 1987) Measured With the MultiGAS (This Study) or by Direct Gas Sampling (Literature Data) in Gas Plumes at El Chichón and Viti M         Case Ratios and $R_{H}$ (Giggenbach, 1987) Measured With the MultiGAS (This Study) or by Direct Gas Sampling (Literature Data) in Gas Plumes at El Chichón and Viti M         Elake—diffuse degassing $40-5.3 \times 10^{-1} (4.7 \times 10^{-1})$ $615-5685 (2,042)$ $0.8-14.5 (5.3)$ $0.6-32 (12)$ $167-1.429 (333)$ $-3.2 \text{ to } -2.7$ Lake—bubbling gas $3-15 \times 10^{-2} (7 \times 10^{-3})$ $1,330-5,090 (2.637)$ $3.4-33 (1.48)$ $0.5-44 (2.2)$ $167-1.429 (333)$ $-3.2 \text{ to } -2.7$ Humatoles $1-7 \times 10^{-3} (16 \times 10^{-3})$ $1,330-5,090 (2.637)$ $3.4-33 (1.6)$ $0.2-3.25 (0.97)$ $9.7-67 (100)$ $-2.4 \text{ to } -0.4$ Fumaroles $1-7 \times 10^{-3} (16 \times 10^{-3})$ $15-291$ $0.1-5.7$ $0.2-142, 2.5-643.3$ $17-333$ $-4.2 \text{ to } -1.1$ Fumaroles $1-7 \times 10^{-3} (16 \times 10^{-3})$ $13-33 (23)$ $0.03-1.3 (1.6)$ $0.2-142, 2.5-643.3$ $17-333$ $-4.2 \text{ to } -1.1$ Fumaroles $1-7 \times 10^{-3} (16 \times 10^{-3})$ $15-291$ $0.1-5.7$ $0.2-142, 2.5-643.3$ $17-333$ $-4.2 \text{ to } -1.1$ Fumaroles $1-7 \times 10^{-3} (12, 7)$ $13-260 (100)$ $3.7 \times$

El Chichón lake gases (bubbling and diffuse) plot at higher  $CO_2/H_2S$  and  $SO_2/H_2S$  ratios than this hydrothermal end-member (Figure 2a). The lake gases  $CO_2/H_2S$  ratios (615–5685) are 30 to 400 times higher than in fumaroles. Similarly, bubbling and diffuse lake gases have distinct  $SO_2/H_2S$  ratios (of, respectively, 0.03–0.15 and 0.4–0.53), but consistently above the fumarolic range (Figure 2a and Table 1).  $H_2/H_2S$  ratios are also higher in the El Chichón lake gas (0.8 to 35) than in the fumaroles (0.08 to 0.5; Figure 2b).

For Víti, a similar trend as for El Chichón is observed, with lake gases plotting at higher  $SO_2/H_2S$ ,  $CO_2/H_2S$ , and  $H_2/H_2S$  compositions than fumaroles (Figures 2a and 2b).

# 4. Discussion

# 4.1. Inefficient Gas Dissolution and Oxidation in Steam-Heated Lakes

At both El Chichón and Víti, we find higher  $CO_2/H_2S$  and  $H_2/H_2S$  ratios in lake gases than in lake-shore fumaroles (Figure 2b). Higher  $CO_2/H_2S$  and  $H_2/H_2S$  ratios may be justified by either (i)  $CO_2$  and  $H_2$  addition in the lake or (ii) preferential  $H_2S$ removal to the lake water aqueous phase.  $CO_2/H_2$  ratios from fumarole and lake gases (bubbling and diffuse) vary within the same range (59–1429 for El Chichón and 20–250 for Víti), suggesting that dissolution in acidic lakes poorly affects these gases (Badrudin, 1994; Shinohara et al., 2010). At the shallow El Chichón lake, Mazot et al. (2011) argued that the  $CO_2$  flux emitted at the lake surface is very similar to the flux entering at the bottom. From our results, we can therefore estimate the fraction of  $H_2S$  and  $H_2$  (x[%]) feeding lake that are ultimately degassed at El Chichón lake surface, using the relation:

$$x[\%] = \left[ (CO_2/x)_{in} / (CO_2/x)_{out} \right] \times 100 \tag{1}$$

where x is either H<sub>2</sub>S or H<sub>2</sub> and  $(CO_2/x)_{in}$  and  $(CO_2/x)_{out}$  are the gas ratios measured in fumaroles and lake gases, respectively. We evaluate that, on average, 1.1% (range, 0.2–5.4%) of the H<sub>2</sub>S entering the lake bottom is ultimately flushing through the lake and discharged in the atmospheric plume. For H<sub>2</sub>, the surface degassed fractions range 68% (range, 30–100%) in bubbling areas and 30% (4–100%) in nonbubbling areas.

While thus  $H_2S$  dissolution in, and oxidation by, the lake (Symonds et al., 2001) is clearly supported by the higher (than fumaroles) lake gas  $CO_2/H_2S$  and  $H_2/H_2S$ ratios, the systematic  $H_2S$  in-plume detection at both volcances implies  $H_2S$  oxidative dissolution is not complete. The rate of  $H_2S$  dissolution into lake-water depends on initial bubble size, lake water depth, and composition. We argue that transit of the feeding gas through both lakes is rapid enough to cause incomplete  $H_2S_{(g)}$  removal, while more efficient dissolution and oxidation would only occur for longer gas residence times in the lake. Considering the similar fumarolic  $CO_2/H_2S$  ratios observed at both volcances, our results suggest more efficient  $H_2S$  escape in the deeper Víti lake than in the shallower El Chichón lake. We argue that El Chichón lake is probably better mixed and oxygenized than Víti lake, leading to higher rates of  $H_2S$  oxidation in the former.

# 4.2. Gas Fluxes

In 2016, the surface area of El Chichón crater lake was estimated at  $1.54 \times 10^5$  m<sup>2</sup>, and the bubbling degassing area was estimated visually to be maximum 20% of the lake surface. In order to roughly estimate the CO<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub> fluxes for the lake, we used the last available CO<sub>2</sub> flux data for April 2015 (Jácome Paz et al., 2016), assuming that the specific (per unit surface area) CO<sub>2</sub> flux has not changed

Table

significantly since 2015 for each degassing population (bubbling versus diffuse degassing). The mean CO<sub>2</sub> flux for the lake in 2016 was estimated at 223 t/day (90% confidence interval of the mean 203–253 t/day), based on a CO<sub>2</sub> flux of 3594 g  $\cdot$  m<sup>-2</sup>  $\cdot$  day<sup>-1</sup> for bubbling gas and 913 g  $\cdot$  m<sup>-2</sup>  $\cdot$  day<sup>-1</sup> for diffuse degassing in 2015 (Jácome Paz et al., 2016). By scaling to the CO<sub>2</sub>/H<sub>2</sub>S and CO<sub>2</sub>/H<sub>2</sub> ratios, and using the mean CO<sub>2</sub> flux for each degassing population (i.e., 111 and 112 t/day for bubbling and diffuse degassing, respectively), we calculated a maximum H<sub>2</sub>S fluxes from El Chichón crater lake between 0.02 and 0.21 t/day. Considering that H<sub>2</sub>S is preferentially emitted in bubbling areas and not detected by the Multi-GAS at the entire diffusive lake area, a more realistic flux would be 0.02–0.06 t/day. For comparison, recent surveys conducted by one of us (M. P. Jácome-Paz) in 2014 and 2015, using a floating accumulation chamber (West System, 2012) equipped with an electrochemical cell (WS-TOX-H2S, underestimation of 5% of H<sub>2</sub>S fluxes; West System, 2012), yielded a H<sub>2</sub>S lake flux of ~0.007 t/day with mean values of 0.03 g  $\cdot$  m<sup>-2</sup>  $\cdot$  day<sup>-1</sup>. We also estimate the H<sub>2</sub> flux (in 2016) in the 0.01 to 0.1 t/day range.

Our  $H_2S$  fluxes are in the same order of magnitude as those estimated for the similarly large, but more active, Ruapehu Crater Lake (New Zealand; Werner et al., 2006). Kawah Ijen released 75 t/day of  $H_2S$  in September 2014 (Gunawan et al., 2016), but this flux includes the  $H_2S$  originating from the 400 °C fumarolic field, in addition to the crater lake. Compared to open-conduit and high-T fumarolic degassing volcanoes (Etna, Stromboli, Vulcano),  $H_2S$  fluxes at El Chichón are, unsurprisingly, at least an order of magnitude lower (Aiuppa, Inguaggiato, et al., 2005). Tamburello et al. (2015) reports a  $H_2$  flux of 3.3 t/day for the peak-activity (posteruptive) crater lake of Copahue (Argentina). Etna emits 1.8 t/day of  $H_2$  (Aiuppa et al., 2011), 1 to 2 orders of magnitude higher than El Chichón. Both Etna and Copahue are actively degassing volcanoes, whereas El Chichón passes a stage of quiescent degassing.

In summary, the  $H_2S$  (and  $H_2$ ) fluxes sustained by acidic (pH ~2–3) crater lakes are relatively minor compared to more active volcanic systems, with or without crater lake, but their cumulative contribution may not be trivial globally, and requires full consideration in future assessments of the global volcanic  $H_2S$  budget.

#### 4.3. Physical-Chemical Model of SO<sub>2</sub> Degassing

The detection of SO<sub>2</sub> in lake gases (Figure 1d), and the SO<sub>2</sub>/H<sub>2</sub>S increase from fumaroles to lake gases (Figure 2a), are more puzzling. Previous studies demonstrated that SO<sub>2</sub> is released by hyperacidic crater lakes (pH near 0 or below; de Moor et al., 2016; Gunawan et al., 2016; Shinohara et al., 2015; Tamburello et al., 2015). El Chichón and Víti crater lakes are not hyperacidic (pH 2–3); however, SO<sub>2</sub> is released from their surfaces. Compositions of fumaroles reported in literature (Mazot et al., 2011; Taran et al., 1998; Tassi et al., 2003) and H<sub>2</sub>/H<sub>2</sub>O ratios measured in this study (reported as  $R_H$  in Table 1) strongly suggest the presence of a reduced hydrothermal system, hence, with H<sub>2</sub>S as the dominant S-gas species (Giggenbach, 1987). As magmatic SO<sub>2</sub> is virtually absent in the parental feeding gas, these observations imply that SO<sub>2</sub> is produced in the shallow, oxidizing lake-fumarole environment.

Casas et al. (2016) recently published the first detailed study of S speciation in El Chichón lake surface waters. In order of abundance, they identified  $S^{2-}$  (<0.77%),  $SO_3^{2-}$  (<3.61%),  $S_4O_6^{2-}$  (<33.2%), and  $SO_4^{2-}$  (<85.2%). No  $S_2O_3^{2-}$  was detected. As we measured  $H_2S_{(g)}$  with the Multi-GAS, we should also add  $H_2S_{(aq)}$  to the dissolved species, since its oxidation reaction:

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$$
 (2)

although being the dominant mechanism generating sulfate in "steam-heated" pools (Rouwet et al., 2008), appears not go to completion in our case.

In analogy with results demonstrating SO<sub>2</sub> production in acid sulfate-rich soils (pH near 4; Macdonald et al., 2004), we propose sulfites as the potential SO<sub>2</sub> source in steam-heated lakes. Notably, our highest SO<sub>2</sub> gas concentrations are detected right above vigorously bubbling degassing areas at El Chichón crater lake, where higher sulfite concentrations have consistently been observed by Casas et al. (2016).

Macdonald et al. (2004) identified a positive correlation between soil evaporation rate (and moisture) and SO<sub>2</sub> emission rates. They concluded that evaporation is the process that liberates gas from soil solutions. This process can be extended to evaporative degassing from acidic lakes, where SO<sub>2</sub> peaks in lake measurements



correlate with H<sub>2</sub>O peaks (Figure S2b). By analogy, in pH 2–3 crater lakes, SO<sub>2</sub> can be produced from sulfites following the equilibria (Barnett, 1985; Barnett & Davis, 1983; Macdonald et al., 2004):

$$H^{+}_{(aq)} + SO_{3}^{2-}_{(aq)} = HSO_{3}^{-}_{(aq)}$$
 (3)

$$H^{+}_{(aq)} + HSO_{3}^{-}_{(aq)} = SO_{2} \cdot H_{2}O_{(l)}$$
(4)

$$SO_2 \cdot H_2O_{(I)} = SO_{2(g)} + H_2O_{(g)}$$
 (5)

Sulfite  $(SO_3^{2-})$  in acid aqueous solutions is generated by  $H_2S$  oxidation, following the reactions (Morse et al., 1987):

$$H_2S_{(aq)} = H^+_{(aq)} + HS^-_{(aq)}$$
 (6)

$$HS^{-}_{(aq)} + 1.5O_{2(aq)} = SO_{3}^{2^{-}}_{(aq)} + H^{+}_{(aq)}$$
<sup>(7)</sup>

or via (Delmelle & Bernard, 2015, and references herein)

$$2H_2S_{(aq)} + 2O_{2(aq)} = S_2O_3^{2-}{}_{(aq)} + H_2O_{(l)} + 2H^{+}{}_{(aq)}$$
(8)

followed by the rapid breakdown of thiosulfate  $(S_2O_3^{2-})$  into sulfite (Delmelle & Bernard, 2015):

$$S_2 O_3^{2-}{}_{(aq)} = S^\circ + S O_3^{2-}{}_{(aq)}$$
 (9)

which is not thermodynamically favored at 29 °C (Table S2).

Under high-temperature and acidic conditions, an alternative reaction pathway is rapid thiosulfate oxidation to tetrathionate ( $S_4O_6^{2-}$ ; Delmelle & Bernard, 2015):

$$2S_2O_3^{2-}{}_{(aq)} + 0.5O_{2(aq)} + 2H^{+}{}_{(aq)} = S_4O_6^{2-}{}_{(aq)} + H_2O_{(I)}$$
(10)

Despite the fact that sulfite is considered highly unstable through reaction (3) and

$$SO_3^{2^-}{}_{(aq)} + 0.5O_{2(aq)} = SO_4^{2^-}{}_{(aq)}$$
 (11)

its presence in El Chichón lake water (Casas et al., 2016) suggests its continuous re-supply via H<sub>2</sub>S oxidation (reactions (6)–(9)).

We use simple thermodynamic calculations to test if sulfite dissolved in the lake is a plausible source for lake gas SO<sub>2</sub>. Equilibrium constants of reactions (2)–(11) at 29 °C are listed in Table S2, and are taken from the EQ3NR code database (Wolery, 1992). Using equilibrium constants for reactions (3)–(5), we calculate the SO<sub>2</sub> partial pressure (pSO<sub>2</sub>) at equilibrium with a dissolved sulfite concentrations of  $3.46 \times 10^{-5}$  mol/L (the lowest measured by Casas et al., 2016). At 29 °C and pH = 2.7, the equilibrium pSO<sub>2</sub> is 0.14 atm, more than 5 orders of magnitude higher than the maximal pSO<sub>2</sub> measured with the Multi-GAS (0.28 µatm) above the El Chichón lake. From these calculations, we conclude that the measured in plume SO<sub>2</sub> can be easily accounted for by dissolved sulfite. In view of the modeled pSO<sub>2</sub> largely exceeding the measured pSO<sub>2</sub>, we additionally argue that (i) only a small fraction of the "measured" dissolved SO<sub>3</sub><sup>2-</sup> is ultimately available (perhaps for kinetic reasons) for participating into reactions (3) and (4) and/or (ii) that large part of the produced SO<sub>2(aq)</sub> is rapidly oxidized to sulfate before being outgassed as SO<sub>2(g)</sub>. Similar calculations show that dissolved pH<sub>2</sub>S at equilibrium with the Multi-GAS (0.3–6.48 µatm), reinforcing the hypothesis that sulfur speciation is not at equilibrium with the pH-redox conditions of the lake. Kaasalainen and Stefánsson (2011) argue that sulfur speciation is controlled by kinetics and not by redox equilibrium.

In view of the above, we propose that, in a dynamic lake-water environment, the continuous supply of H<sub>2</sub>S from the underlying hydrothermal system initiates a kinetically driven, oxidative mechanism with sulfite as



a transient species, and SO<sub>2</sub>-gas and dissolved sulfate as the final products. During this process, H<sub>2</sub>S is only partially sequestered by the lake, and is in small part degassed via the lake gas.

Despite the fact that SO<sub>2</sub> concentrations are higher above bubbling areas than in diffuse degassing areas, the opposite is observed for SO<sub>2</sub>/H<sub>2</sub>S ratios (diffusive > bubbling). This can be explained by (i) lower H<sub>2</sub>S<sub>(g)</sub> dissolution or (ii) reaction (10) dominating thiosulfate breakdown in bubbling areas. In areas of active gas transport through bubbles, gas dissolution into shallow lakes is physically delayed and limited (e.g., Caudron et al., 2012). Consequently, H<sub>2</sub>S dissolution is less efficient for bubbling areas of lakes and pools, leading to lower SO<sub>2</sub>/H<sub>2</sub>S ratios in their degassing plumes. Moreover, if we assume ubiquitous presence of sulfites, SO<sub>2</sub> production occurs in the entire lake through reactions (7) and (9). Considering the absence of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and magmatic SO<sub>2</sub>, and the abundance of S<sub>4</sub>O<sub>6</sub><sup>2-</sup> in the lake (Casas et al., 2016), it can be argued that, in hot bubbling areas, thiosulfate is preferentially decomposed into tetrathionate (reaction (10)), relative to nonbubbling and colder areas.

As  $SO_2$  is also measured at Víti, arguably the same chemical processes occur to form  $SO_2$  from this originally  $H_2S$ -dominated lake system. Unfortunately, S speciation has so far not been reported for Víti to confirm our hypothesis.

## 5. Conclusions and Implications for Monitoring

We have found clear evidence of H<sub>2</sub>S release from steam-heated lakes. Our results thus point to incomplete H<sub>2</sub>S dissolution and oxidation by lake water in acidic (pH 2–3) shallow crater-lake conditions. Trace amount of SO<sub>2</sub> in degassing plumes coming off nonhyperacid crater lakes was also measured for the first time. Both steam-heated lakes are fed by reduced H<sub>2</sub>S-rich fluids entering from the underlying hydrothermal system, without the direct input of magmatic SO<sub>2</sub>. Therefore, physical-chemical processes inside the lake's water body cause SO<sub>2</sub> formation, although in small amounts. Combining S-speciation results for El Chichón lake water with our in-plume gas measurements, we proposed that SO<sub>2</sub> is formed by H<sub>2</sub>S oxidation via sulfite as the transient S species. Our observations highlight that sulfur degassing through pH 2–3 lakes is a highly kinetic, nonequilibrium process. The original H<sub>2</sub>S is partially oxidized in the lake water (mainly as SO<sub>4</sub><sup>2-</sup>), and partially released as a gas phase, as H<sub>2</sub>S or SO<sub>2</sub>, together with the abundant CO<sub>2</sub> and poorly reactive H<sub>2</sub>.

More work is required to better constrain kinetics of this degassing process, arguably very fast. It appears that the various S species are transient solutes strongly affected by S-rich (SO<sub>2</sub> and H<sub>2</sub>S) gas flushing through lakes. This kinetics seems to be independent of the "residence time-dependent monitoring time window" (Rouwet et al., 2014), defined for "slower" solutes, such as Mg<sup>2+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. As the definition of a time window is crucial in volcano monitoring, ideally fitting the time frame of the volcanic feature we aim to forecast, we strongly suggest combining the total S speciation with gas chemistry (reactive and nonreactive gas species) at the interface between lake and atmosphere. Controlling parameters in experimental setups (e.g., lake water T, pH, bubbling versus nonbubbling, lake depth,  $f_{O2}$ ) can also help to quantify and time-frame the degassing process.

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