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Key Points:

- H₂S dissolution and oxidation is inefficient in pH 2–3 lakes
- Sulfur degassing through pH 2–3 lakes is a kinetically driven process
- SO₂ degassed from pH 2–3 lakes originates from H₂S oxidation with sulfites as transient species

Supporting Information:

- Data S1
- Table S1

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

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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 H₂S and SO₂ are degassed by these pH 2–3 lakes. We find higher CO₂/H₂S and H₂/H₂S 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 H₂S_(g) contributed by the subaquatic fumaroles ultimately reaches the atmosphere. At El Chichón, we estimate a H₂S output from the crater lake of 0.02–0.06 t/day. Curiously, SO₂ is also detected at trace levels in the gases released from both lakes (0.003–0.3 ppmv). We propose that H₂S supplied into the lakes initiates a series of complex oxidation reactions, having sulfite as an intermediate product, and ultimately leading to SO₂ 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 SO₂, 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 (SO₂ and H₂S) in the plumes of less acidic (pH 2–3) lakes El Chichón (Mexico) and Víti (Iceland). Our results demonstrate that H₂S, coming from the sublittoral hydrothermal systems is only partially dissolved and oxidized by the lake water. In addition, we discover trace amount of SO₂ coming off both lakes. We propose that SO₂ is produced into the lake by H₂S 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 SO₂ 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 hyperacidic 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 (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

($T = 52\text{--}58\text{ }^{\circ}\text{C}$) and highly acidic ($\text{pH} = 0.56$) lake appeared on the crater floor (Casadevall et al., 1984) that has changed (in 2016, $T \sim 30\text{ }^{\circ}\text{C}$ and $\text{pH} \sim 2.75$) 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 ($65^{\circ}02'\text{N}$, $16^{\circ}43'\text{W}$), 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, $\sim 1.54 \times 10^5\text{ m}^2$ for El Chichón and $\sim 7.8 \times 10^3\text{ m}^2$ for Víti) steam-heated pools where dissolved oxidized sulfur compounds originate mainly from oxidation of H_2S sourced at the lake bottom (maximum depth $\sim 4.5\text{ m}$ at El Chichón and $\sim 60\text{ m}$ 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 $\text{pH} \sim 2\text{--}3$ 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 et al., 2005; Shinohara, 2005). We used a compact sensor unit containing a nondispersive infrared spectrometer (for CO_2 ; range = $0\text{--}3000\text{ ppm}$), three electrochemical gas sensors for H_2S (range = $0\text{--}100\text{ ppm}$), SO_2 (range = $0\text{--}200\text{ ppm}$), and H_2 (range = $0\text{--}200\text{ ppm}$) and a relative humidity sensor (range = $0\text{--}100\%$) for indirectly measuring H_2O . 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 ($\text{pH} 4\text{--}6$; 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 $30\text{--}40\text{ cm}$ 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 Víti lake. This latter configuration allows for the detection of very low SO_2 concentrations ($\ll 1\text{ ppmv}$; see Figure S2), but is complicated by the rapid saturation of the CO_2 , H_2S , and H_2 sensors. Moreover, as the relative humidity increases inside the funnel with time, functioning of electrochemical sensors (SO_2 , H_2S , H_2) 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_2 Detection

The pH (2.76 ± 0.37), temperature ($21.8 \pm 1.16\text{ }^{\circ}\text{C}$), 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 $30.1 \pm 1\text{ }^{\circ}\text{C}$ (chemical composition at the lake center is detailed in Table S1).

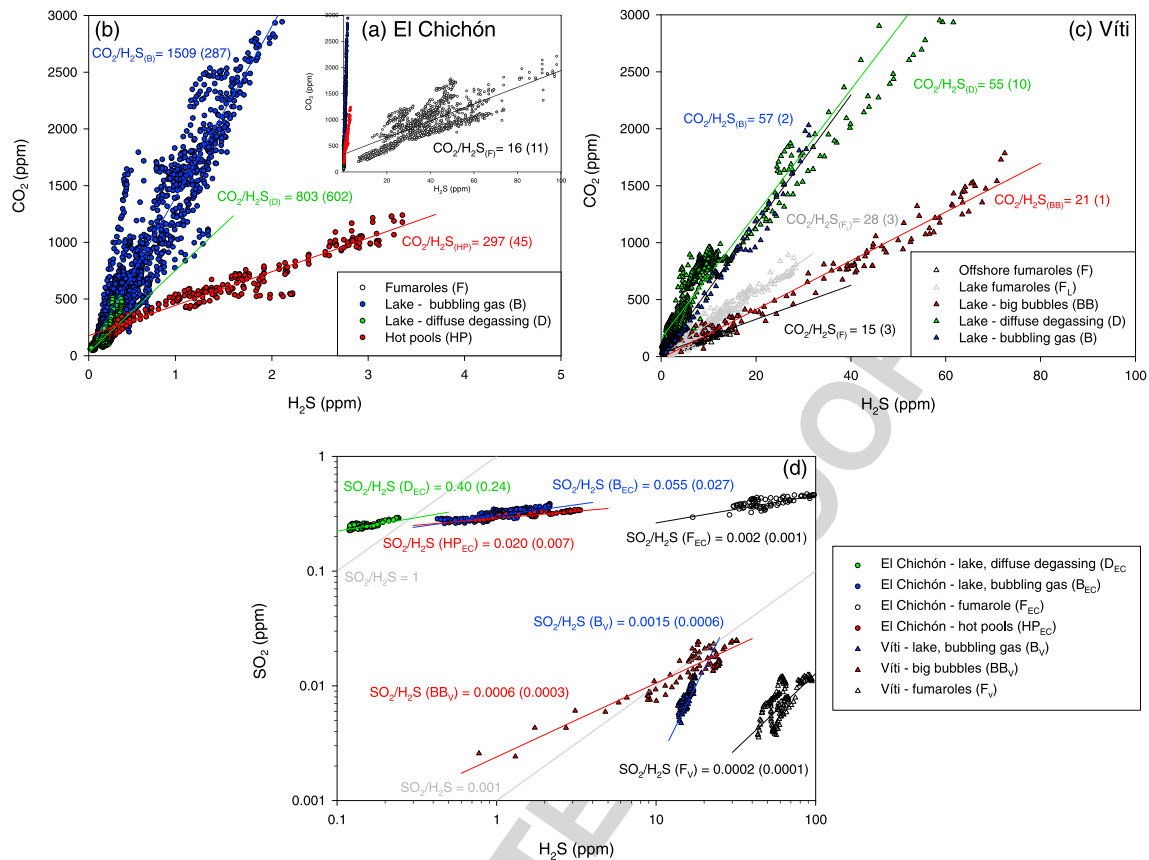


Figure 1. Examples of CO₂ versus H₂S scatterplots at (a and b) El Chichón and (c) Viti and of SO₂ versus H₂S scatterplots at (d) both volcanoes. Ratios values corresponding to the regression lines are written in the plots with their errors in parenthesis. Plot (c) shows the fumarolic composition (CO₂/H₂S 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 Viti (called lake-big bubbles). In the paper, those ratios are therefore assimilated to fumaroles. Plot (d) illustrates the lower SO₂ concentrations measured at Viti compared to El Chichón but also the increase of the SO₂/H₂S ratio as followed: Fumaroles < hot pools < bubbling lake gas < diffuse degassing.

Fumarole gases, pool gases, and lake gases at both volcanoes were dominated by H₂O and CO₂ (10–1000s of ppmv). H₂S (up to ~7 ppmv at El Chichón and at ~100 ppmv at Viti) and H₂ (up to 50 and 70 ppmv at El Chichón and Viti, respectively) were unambiguously measured in the lake gases at both lakes (Figures 1a–1c). Small amounts of SO₂ in the lake gases of both volcanoes (<0.3 and <0.003 ppmv for El Chichón and Viti, respectively; see Figure 1d) were also measured.

We caution that, given the low concentrations measured, well below the typical calibration range of SO₂ sensor (1–100 ppmv), our SO₂ ratios should not be viewed as truly quantitative for this gas. However, our SO₂ concentrations exhibit a positive correlation ($R^2 > 0.6$) with H₂S (Figure 1d), CO₂, and H₂O (Figure S2b), strongly suggesting that the SO₂ peaks are real, and not artifacts due to the sensor's noise. In addition, based on laboratory tests using 50–100-ppmv H₂S standard gases, we did not stimulate false SO₂ signals with H₂S gas (cross-sensitivity to H₂S of the SO₂ sensor is 0 according to our laboratory tests). As such, our El Chichón and Viti results should be intended as reflecting that SO₂ 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 SO₂, and interpreted its presence as not being magmatic, but rather due to secondary processes (i.e., saline water droplets in the collecting bottles). At Viti, very low SO₂ 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 SO₂ in lake and pool gases is unusual. No SO₂ has previously been measured in gases emitted

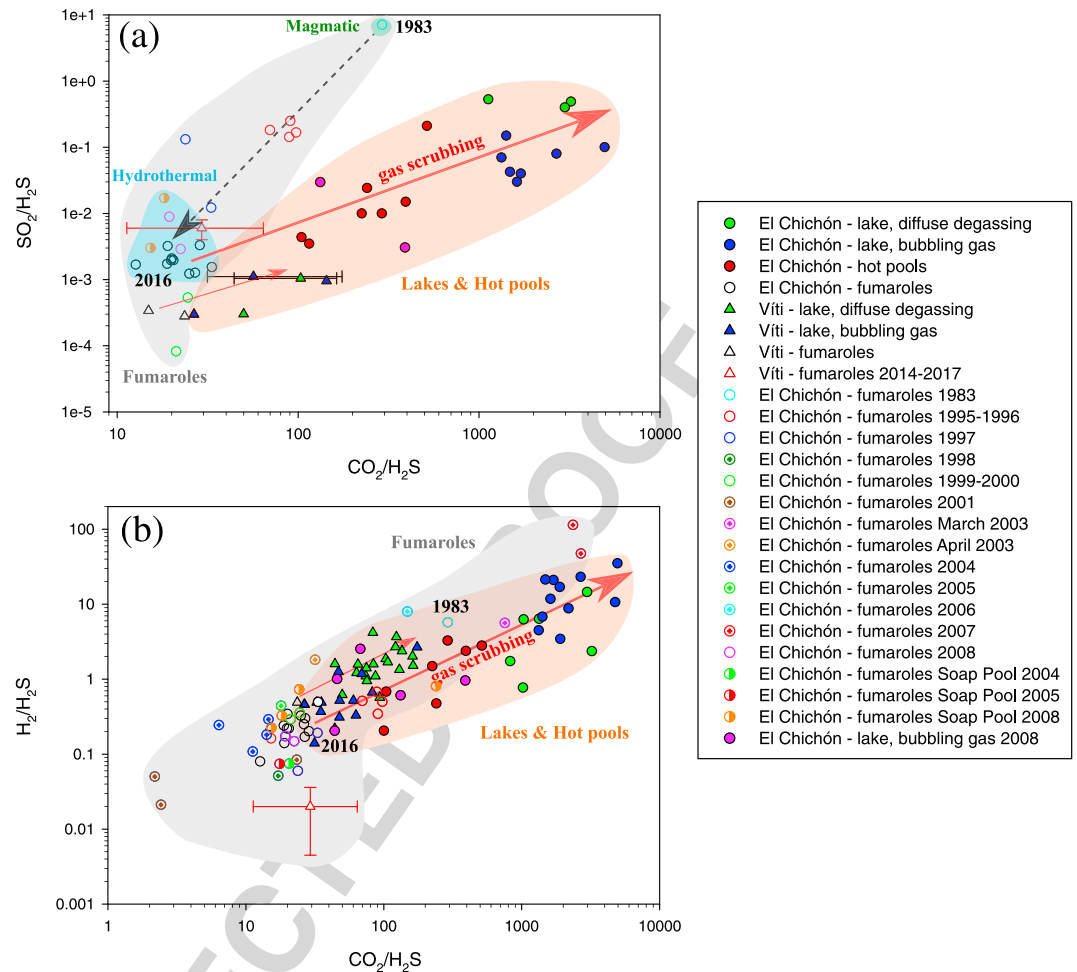


Figure 2. (a) $\text{SO}_2/\text{H}_2\text{S}$ versus $\text{CO}_2/\text{H}_2\text{S}$ ratios and (b) $\text{H}_2/\text{H}_2\text{S}$ versus $\text{CO}_2/\text{H}_2\text{S}$ ratios measured in El Chichón and Viti plumes. Data references are listed in Table 1. The ratios symbolized by empty circles with a cross inside correspond to H_2 or CO_2 versus total sulfur instead of H_2S . At both volcanoes, 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 $\text{SO}_2/\text{H}_2\text{S}$ and $\text{CO}_2/\text{H}_2\text{S}$ ratios through time at El Chichón (black arrow). Since 2008, the fumarolic $\text{SO}_2/\text{H}_2\text{S}$ (10^{-2} to 10^{-3}), $\text{CO}_2/\text{H}_2\text{S}$ (13–33), and $\text{H}_2/\text{H}_2\text{S}$ (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 $\text{SO}_2/\text{H}_2\text{S}$ versus $\text{CO}_2/\text{H}_2\text{S}$ and $\text{H}_2/\text{H}_2\text{S}$ versus $\text{CO}_2/\text{H}_2\text{S}$. El Chichón and Viti 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 $\text{SO}_2/\text{H}_2\text{S}$ and $\text{CO}_2/\text{H}_2\text{S}$ 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 ($\text{SO}_2/\text{H}_2\text{S} = 7$, $\text{CO}_2/\text{H}_2\text{S} = 291$) to more hydrothermal compositions soon after (Taran et al., 1998; Tassi et al., 2003). Since 2008, fumarolic $\text{CO}_2/\text{H}_2\text{S}$ ratios have clustered at values (13–33) representative of hydrothermal conditions, whereas $\text{SO}_2/\text{H}_2\text{S}$ ratios have shown larger spread (10^{-2} to 10^{-3} ; Figure 2a). This H_2S -rich hydrothermal gas is assumed to be a proxy for the composition of the subaquatic fumaroles feeding the lake today.

Table 1
Range of 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 Volcanoes

Volcano	Plume type	SO ₂ /H ₂ S	CO ₂ /H ₂ S	H ₂ /H ₂ S	H ₂ O/CO ₂	CO ₂ /H ₂	R _H	Reference
El Chichón	Lake—diffuse degassing	4.0–5.3 × 10 ⁻¹ (4.7 × 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 × 10 ⁻² (7 × 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 × 10 ⁻³ (16 × 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 × 10 ⁻³ (3 × 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 × 10 ⁻⁴	15–291	0.1–5.7	0.2–142, 2.5–84.3 ^b (between 1996 and 2005)	17–333	-4.2 to -1.1	Casadevall et al. (1984), Tassi et al. (2003), Mazot et al. (2011), and CCVG	
Viti	Strongly bubbling gas (2008)	3 × 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 × 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 × 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 ^a	28–34 × 10 ⁻⁵ (31 × 10 ⁻⁵)	15–27 (22)	0.23–0.49 (0.39)	5 (±1.3 ^c)	48–67 (56)	-2.5	This study
Fumaroles (2014–2017)	4–8 × 10 ⁻³ (6 × 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	

Note. The values in parenthesis are the means.
^aIt includes the offshore fumaroles but also the shallow subaqueous fumaroles close to the shore (see Figures 1c and 1d for explanation).
^bThe fumaroles before 1996 have higher temperature than 98 °C and in 2008 the water vapor was mostly condensed in the sampling fumarolic gas. Therefore, they cannot be used to compare to the present H₂O/CO₂ ratios.
^cError.

El Chichón lake gases (bubbling and diffuse) plot at higher CO₂/H₂S and SO₂/H₂S ratios than this hydrothermal end-member (Figure 2a). The lake gases CO₂/H₂S ratios (615–5685) are 30 to 400 times higher than in fumaroles. Similarly, bubbling and diffuse lake gases have distinct SO₂/H₂S ratios (of, respectively, 0.03–0.15 and 0.4–0.53), but consistently above the fumarolic range (Figure 2a and Table 1). H₂/H₂S 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 Viti, a similar trend as for El Chichón is observed, with lake gases plotting at higher SO₂/H₂S, CO₂/H₂S, and H₂/H₂S 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 Viti, we find higher CO₂/H₂S and H₂/H₂S ratios in lake gases than in lake-shore fumaroles (Figure 2b). Higher CO₂/H₂S and H₂/H₂S ratios may be justified by either (i) CO₂ and H₂ addition in the lake or (ii) preferential H₂S removal to the lake water aqueous phase. CO₂/H₂ ratios from fumarole and lake gases (bubbling and diffuse) vary within the same range (59–1429 for El Chichón and 20–250 for Viti), 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 CO₂ 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 H₂S and H₂ (x[%]) feeding lake that are ultimately degassed at El Chichón lake surface, using the relation:

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

where x is either H₂S or H₂ and (CO₂/x)_{in} and (CO₂/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 H₂S entering the lake bottom is ultimately flushing through the lake and discharged in the atmospheric plume. For H₂, the surface degassed fractions range 68% (range, 30–100%) in bubbling areas and 30% (4–100%) in nonbubbling areas.

While thus H₂S dissolution in, and oxidation by, the lake (Symonds et al., 2001) is clearly supported by the higher (than fumaroles) lake gas CO₂/H₂S and H₂/H₂S ratios, the systematic H₂S in-plume detection at both volcanoes implies H₂S oxidative dissolution is not complete. The rate of H₂S 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 H₂S(g) removal, while more efficient dissolution and oxidation would only occur for longer gas residence times in the lake. Considering the similar fumarolic CO₂/H₂S ratios observed at both volcanoes, our results suggest more efficient H₂S escape in the deeper Viti lake than in the shallower El Chichón lake. We argue that El Chichón lake is probably better mixed and oxygenized than Viti lake, leading to higher rates of H₂S oxidation in the former.

4.2. Gas Fluxes

In 2016, the surface area of El Chichón crater lake was estimated at 1.54 × 10⁵ m², and the bubbling degassing area was estimated visually to be maximum 20% of the lake surface. In order to roughly estimate the CO₂, H₂S, and H₂ fluxes for the lake, we used the last available CO₂ flux data for April 2015 (Jácome Paz et al., 2016), assuming that the specific (per unit surface area) CO₂ flux has not changed

significantly since 2015 for each degassing population (bubbling versus diffuse degassing). The mean CO₂ 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 CO₂ flux of 3594 g · m⁻² · day⁻¹ for bubbling gas and 913 g · m⁻² · day⁻¹ for diffuse degassing in 2015 (Jácome Paz et al., 2016). By scaling to the CO₂/H₂S and CO₂/H₂ ratios, and using the mean CO₂ flux for each degassing population (i.e., 111 and 112 t/day for bubbling and diffuse degassing, respectively), we calculated a maximum H₂S fluxes from El Chichón crater lake between 0.02 and 0.21 t/day. Considering that H₂S 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 H₂S fluxes; West system, 2012), yielded a H₂S lake flux of ~0.007 t/day with mean values of 0.03 g · m⁻² · day⁻¹. We also estimate the H₂ flux (in 2016) in the 0.01 to 0.1 t/day range.

Our H₂S 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 H₂S in September 2014 (Gunawan et al., 2016), but this flux includes the H₂S 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), H₂S fluxes at El Chichón are, unsurprisingly, at least an order of magnitude lower (Aiuppa et al., 2005). Tamburello et al. (2015) reports a H₂ flux of 3.3 t/day for the peak-activity (post-eruptive) crater lake of Copahue (Argentina). Etna emits 1.8 t/day of H₂ (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 H₂S (and H₂) 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 H₂S budget.

4.3. Physical-Chemical Model of SO₂ Degassing

The detection of SO₂ in lake gases (Figure 1d), and the SO₂/H₂S increase from fumaroles to lake gases (Figure 2a), are more puzzling. Previous studies demonstrated that SO₂ 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 Viti crater lakes are not hyperacidic (pH 2–3); however, SO₂ is released from their surfaces. Compositions of fumaroles reported in literature (Mazot et al., 2011; Taran et al., 1998; Tassi et al., 2003) and H₂/H₂O ratios measured in this study (reported as R_H in Table 1) strongly suggest the presence of a reduced hydrothermal system, hence, with H₂S as the dominant S-gas species (Giggenbach, 1987). As magmatic SO₂ is virtually absent in the parental feeding gas, these observations imply that SO₂ 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 S²⁻ (<0.77%), SO₃²⁻ (<3.61%), S₄O₆²⁻ (<33.2%), and SO₄²⁻ (<85.2%). No S₂O₃²⁻ was detected. As we measured H₂S_(g) with the Multi-GAS, we should also add H₂S_(aq) to the dissolved species, since its oxidation reaction:

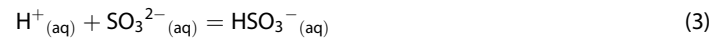


although being the dominant mechanism generating sulfate in “steam-heated” pools (Rouwet et al., 2008), appears not go to completion in our case.

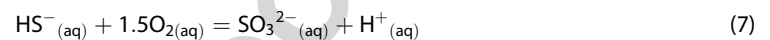
In analogy with results demonstrating SO₂ production in acid sulfate-rich soils (pH near 4; Macdonald et al., 2004), we propose sulfites as the potential SO₂ source in steam-heated lakes. Notably, our highest SO₂ gas concentrations are detected right above vigorously bubbling degassing areas at El Chichón 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 SO₂ 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 SO₂ peaks in lake measurements

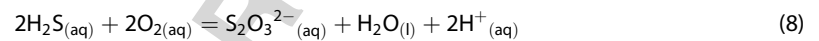
correlate with H₂O peaks (Figure S2b). By analogy, in pH 2–3 crater lakes, SO₂ can be produced from sulfites following the equilibria (Barnett, 1985; Barnett & Davis, 1983; Macdonald et al., 2004):



Sulfite (SO₃²⁻) in acid aqueous solutions is generated by H₂S oxidation, following the reactions (Morse et al., 1987):



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

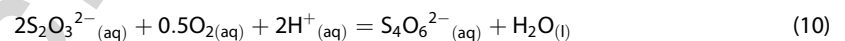


followed by the rapid breakdown of thiosulfate (S₂O₃²⁻) into sulfite (Delmelle & Bernard, 2015):



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 (S₄O₆²⁻; Delmelle & Bernard, 2015):



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



its presence in El Chichón lake water (Casas et al., 2016) suggests its continuous re-supply via H₂S oxidation (reactions (6)–(9)).

We use simple thermodynamic calculations to test if sulfite dissolved in the lake is a plausible source for lake gas SO₂. 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 SO₂ partial pressure (pSO₂) at equilibrium with a dissolved sulfite concentrations of 3.46 × 10⁻⁵ mol/L (the lowest measured by Casas et al., 2016). At 29 °C and pH = 2.7, the equilibrium pSO₂ is 0.14 atm, more than 5 orders of magnitude higher than the maximal pSO₂ measured with the Multi-GAS (0.28 μatm) above the El Chichón lake. From these calculations, we conclude that the measured in plume SO₂ can be easily accounted for by dissolved sulfite. In view of the modeled pSO₂ largely exceeding the measured pSO₂, we additionally argue that (i) only a small fraction of the “measured” dissolved SO₃²⁻ is ultimately available (perhaps for kinetic reasons) for participating into reactions (3) and (4) and/or (ii) that large part of the produced SO_{2(aq)} is rapidly oxidized to sulfate before being outgassed as SO_{2(g)}. Similar calculations show that dissolved pH₂S at equilibrium with the sulfate content of the lake water is significantly lower (4.16 × 10⁻³³ μatm) than the pH₂S measured 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 H₂S from the underlying hydrothermal system initiates a kinetically driven, oxidative mechanism with sulfite as

a transient species, and SO₂-gas and dissolved sulfate as the final products. During this process, H₂S is only partially sequestered by the lake, and is in small part degassed via the lake gas.

Despite the fact that SO₂ concentrations are higher above bubbling areas than in diffuse degassing areas, the opposite is observed for SO₂/H₂S ratios (diffusive > bubbling). This can be explained by (i) lower H₂S_(g) 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, H₂S dissolution is less efficient for bubbling areas of lakes and pools, leading to lower SO₂/H₂S ratios in their degassing plumes. Moreover, if we assume ubiquitous presence of sulfites, SO₂ production occurs in the entire lake through reactions (7) and (9). Considering the absence of S₂O₃²⁻ and magmatic SO₂, and the abundance of S₄O₆²⁻ 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 SO₂ is also measured at Viti, arguably the same chemical processes occur to form SO₂ from this originally H₂S-dominated lake system. Unfortunately, S speciation has so far not been reported for Viti to confirm our hypothesis.

5. Conclusions and Implications for Monitoring

We have found clear evidence of H₂S release from steam-heated lakes. Our results thus point to incomplete H₂S dissolution and oxidation by lake water in acidic (pH 2–3) shallow crater-lake conditions. Trace amount of SO₂ in degassing plumes coming off nonhyperacid crater lakes was also measured for the first time. Both steam-heated lakes are fed by reduced H₂S-rich fluids entering from the underlying hydrothermal system, without the direct input of magmatic SO₂. Therefore, physical-chemical processes inside the lake's water body cause SO₂ formation, although in small amounts. Combining S-speciation results for El Chichón lake water with our in-plume gas measurements, we proposed that SO₂ is formed by H₂S 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 H₂S is partially oxidized in the lake water (mainly as SO₄²⁻), and partially released as a gas phase, as H₂S or SO₂, together with the abundant CO₂ and poorly reactive H₂.

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 (SO₂ and H₂S) 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 Mg²⁺, Cl⁻, and SO₄²⁻. 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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References

- Aiuppa, A., Federico, C., Giudice, G., Giuffrida, G., Guida, R., Gurrieri, S., et al. (2009). The 2007 eruption of Stromboli volcano: Insights from real-time measurement of the volcanic gas plume CO₂/SO₂ ratio. *Journal of Volcanology and Geothermal Research*, 182(3-4), 221–230. <https://doi.org/10.1016/j.jvolgeores.2008.09.013>
- Aiuppa, A., Federico, C., Giudice, G., & Gurrieri, S. (2005). Chemical mapping of a fumarolic field: La Fossa crater, Vulcano island (Aeolian Islands, Italy). *Geophysical Research Letters*, 32(13), L13309. <https://doi.org/10.1029/2005GL023207>
- Aiuppa, A., Giudice, G., Liuzzo, M., Tamburello, G., Allard, P., Calabrese, S., et al. (2012). First volatile inventory for Gorely volcano, Kamchatka. *Geophysical Research Letters*, 39(6), L06307. <https://doi.org/10.1029/2012GL051177>
- Aiuppa, A., Inguaggiato, S., McGonigle, A. J., O'dwyer, M., Oppenheimer, C., Padgett, M. J., et al. (2005). H₂S fluxes from Mt. Etna, Stromboli, and Vulcano (Italy) and implications for the sulfur budget at volcanoes. *Geochimica et Cosmochimica Acta*, 69(7), 1861–1871. <https://doi.org/10.1016/j.gca.2004.09.018>
- Aiuppa, A., Robidoux, P., Tamburello, G., Conde, V., Galle, B., Avarid, G., et al. (2014). Gas measurements from the Costa Rica-Nicaragua volcanic segment suggest possible along-arc variations in volcanic gas chemistry. *Earth and Planetary Science Letters*, 407, 134–147. <https://doi.org/10.1016/j.epsl.2014.09.041>
- Aiuppa, A., Shinohara, H., Tamburello, G., Giudice, G., Liuzzo, M., & Moretti, R. (2011). Hydrogen in the gas plume of an open-vent volcano, Mount Etna, Italy. *Journal of Geophysical Research: Solid Earth*, 116(B10), B10204. <https://doi.org/10.1029/2011JB008461>
- Armienta, M. A., De la Cruz-Reyna, S., & Macías, J. L. (2000). Chemical characteristics of the crater lakes of Popocatepetl, El Chichon, and Nevado de Toluca volcanoes, Mexico. *Journal of Volcanology and Geothermal Research*, 97(1-4), 105–125. [https://doi.org/10.1016/S0377-0273\(99\)00157-2](https://doi.org/10.1016/S0377-0273(99)00157-2)

- Badrudin, M. (1994). Kelut volcano monitoring: Hazards, mitigation and changes in water chemistry prior to the 1990 eruption. *Geochemical Journal*, 28(3), 233–241. <https://doi.org/10.2343/geochemj.28.233>
- Barnett, D. (1985). Sulphites in foods: Their chemistry and analysis. *Food Technology in Australia*, 37, 503–505.
- Barnett, D., & Davis, E. G. (1983). A GC method for the determination of sulphur dioxide in food headspaces. *Journal of Chromatographic Science*, 21(5), 205–208. <https://doi.org/10.1093/chromsci/21.5.505>
- Capaccioni, B., Rouwet, D., & Tassi, F. (2017). HCl degassing from extremely acidic crater lakes: Preliminary results from experimental determinations and implications for geochemical monitoring. *Geological Society, London, Special Publications*, 437(1), 97–106. <https://doi.org/10.1144/SP437.12>
- Carey, R. J., Houghton, B. F., & Thordarson, T. (2009). Abrupt shifts between wet and dry phases of the 1875 eruption of Askja volcano: Microscopic evidence for macroscopic dynamics. *Journal of Volcanology and Geothermal Research*, 184(3–4), 256–270. <https://doi.org/10.1016/j.jvolgeores.2009.04.003>
- Casadevall, T. J., De la Cruz-Reyna, S., Rose, W. I., Bagley, S., Finnegan, D. L., & Zoller, W. H. (1984). Crater lake and post-eruption hydrothermal activity, El Chichón volcano, Mexico. *Journal of Volcanology and Geothermal Research*, 23, 169,179–175,191. [https://doi.org/10.1016/0377-0273\(84\)90061-1](https://doi.org/10.1016/0377-0273(84)90061-1)
- Casas, A. S., Armienta, M. A., & Ramos, S. (2016). Sulfur speciation with high performance liquid chromatography as a tool for El Chichón volcano, crater lake monitoring. *Journal of South American Earth Sciences*, 72, 241–249. <https://doi.org/10.1016/j.jsames.2016.09.001>
- Caudron, C., Mazot, A., & Bernard, A. (2012). Carbon dioxide dynamics in Kelud volcanic lake. *Journal of Geophysical Research: Solid Earth*, 117(B5), B05102. <https://doi.org/10.1029/2011JB008806>
- CCVG Newsletter (2010). *Newsletter of the IAVCEI Commission on the Chemistry of Volcanic Gases*, 2010, 21.
- Clifton, A. E., Pagli, C., Jónsdóttir, J. F., Eythorsdóttir, K., & Vogfjörð, K. (2003). Surface effects of triggered fault slip on Reykjanes peninsula, SW Iceland. *Tectonophysics*, 369(3–4), 145–154. [https://doi.org/10.1016/S0040-1951\(03\)00201-4](https://doi.org/10.1016/S0040-1951(03)00201-4)
- de Moor, J. M., Aiuppa, A., Pacheco, J., Avaró, G., Kern, C., Liuzzo, M., et al. (2016). Short-period volcanic gas precursors to phreatic eruptions: Insights from Poás volcano, Costa Rica. *Earth and Planetary Science Letters*, 442, 218–227. <https://doi.org/10.1016/j.epsl.2016.02.056>
- Delmelle, P., & Bernard, A. (2015). The remarkable chemistry of sulfur in hyper-acid crater lakes: a scientific tribute to bokuichiro takano and minoru kusakabe. In *Dans Volcanic Lakes*, (pp. 239–259). Springer. https://doi.org/10.1007/978-3-642-36833-2_10
- Di Napoli, R., Aiuppa, A., & Allard, P. (2014). First multi-gas based characterisation of the boiling Lake volcanic gas (Dominica, Lesser Antilles). *Annals of Geophysics*, 56, 0559.
- Friðriksson, Á. (2014). What is below the water masses? Multibeam studies of Öskjuvatn, Thingvallavatn and Kleifarvatn (Master's thesis). Retrieved from Skemman. (<http://hdl.handle.net/1946/18548>). Reykjavik, Iceland: University of Iceland.
- Giggenbach, W. F. (1987). Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand. *Applied Geochemistry*, 2(2), 143–161. [https://doi.org/10.1016/0883-2927\(87\)90030-8](https://doi.org/10.1016/0883-2927(87)90030-8)
- Gunawan, H., Caudron, C., Pallister, J., Primulyana, S., Christenson, B., McCausland, W., et al. (2016). New insights into Kawah Ijens volcanic system from the wet volcano workshop experiment. *Geological Society, London, Special Publications*, 437(1), 35–56. <https://doi.org/10.1144/SP437.7>
- Jácome Paz, M. P., Taran, Y., Inguaggiato, S., & Collard, N. (2016). CO₂ flux and chemistry of El Chichón crater lake (México) in the period 2013–2015: Evidence for the enhanced volcano activity. *Geophysical Research Letters*, 43(1), 127–134. <https://doi.org/10.1002/2015gl066354>
- Kaasalainen, H., & Stefánsson, A. (2011). Sulfur speciation in natural hydrothermal waters, Iceland. *Geochimica et Cosmochimica Acta*, 75(10), 2777–2791. <https://doi.org/10.1016/j.gca.2011.02.036>
- Kalacheva, E., Taran, Y., Kótenko, T., Hattori, K., Kótenko, L., & Solis-Pichardo, G. (2016). Volcano-hydrothermal system of Ebeko volcano, Paramushir, Kuril Islands: Geochemistry and solute fluxes of magmatic chlorine and sulfur. *Journal of Volcanology and Geothermal Research*, 310, 118–131. <https://doi.org/10.1016/j.jvolgeores.2015.11.006>
- Macdonald, B. C., Denmead, O. T., White, I., & Melville, M. D. (2004). Natural sulfur dioxide emissions from sulfuric soils. *Atmospheric Environment*, 38(10), 1473–1480. <https://doi.org/10.1016/j.atmosenv.2003.12.005>
- Mazot, A., Rouwet, D., Taran, Y., Inguaggiato, S., & Varley, N. (2011). CO₂ and he degassing at El Chichón volcano, Chiapas, Mexico: Gas flux, origin and relationship with local and regional tectonics. *Bulletin of Volcanology*, 73(4), 423–441. <https://doi.org/10.1007/s00445-010-0443-y>
- Mazot, A., & Taran, Y. (2009). CO₂ flux from the volcanic lake of El Chichón (Mexico). *Geofísica internacional*, 48, 73–83.
- Morse, J. W., Millero, F. J., Cornwell, J. C., & Rickard, D. (1987). The chemistry of the hydrogen sulfide and iron sulfide systems in natural waters. *Earth-Science Reviews*, 24(1), 1–42. [https://doi.org/10.1016/0012-8252\(87\)90046-8](https://doi.org/10.1016/0012-8252(87)90046-8)
- Peiffer, L., Rouwet, D., & Taran, Y. (2015). Fluid geochemistry of El Chichón volcano-hydrothermal system. In *Active Volcanoes of Chiapas (Mexico): El Chichón and Tacaná*, (pp. 77–95). Springer. https://doi.org/10.1007/978-3-642-25890-9_4
- Rodríguez, A., Bergen, M. J., & Eggenkamp, H. G. (2017). Experimental evaporation of hyperacid brines: Effects on chemical composition and chlorine isotope fractionation. *Geochimica et Cosmochimica Acta*, 222, 467–484. <https://doi.org/10.1016/j.gca.2017.10.032>
- Rouwet, D., Bellomo, S., Brusca, L., Inguaggiato, S., Jutzeler, M., Mora, R., et al. (2009). Major and trace element geochemistry of El Chichón volcano-hydrothermal system (Chiapas, Mexico) in 2006–2007: Implications for future geochemical monitoring. *Geofísica internacional*, 48, 55–72.
- Rouwet, D., Christenson, B. W., Tassi, F., & Vandemeulebrouck, J. (2015). *Volcanic Lakes*. Springer. https://doi.org/10.1007/978-3-642-36833-2_1
- Rouwet, D., Taran, Y., Inguaggiato, S., Varley, N., & Santiago, J. A. (2008). Hydrochemical dynamics of the “lake-spring” system in the crater of El Chichón volcano (Chiapas, Mexico). *Journal of Volcanology and Geothermal Research*, 178(2), 237–248. <https://doi.org/10.1016/j.jvolgeores.2008.06.026>
- Rouwet, D., Taran, Y. A., & Varley, N. R. (2004). Dynamics and mass balance of El Chichón crater lake, Mexico. *Geofísica Internacional*, 43, 427–434.
- Rouwet, D., Tassi, F., Mora-Amador, R., Sandri, L., & Chiarini, V. (2014). Past, present and future of volcanic lake monitoring. *Journal of Volcanology and Geothermal Research*, 272, 78–97. <https://doi.org/10.1016/j.jvolgeores.2013.12.009>
- Shinohara, H. (2005). A new technique to estimate volcanic gas composition: Plume measurements with a portable multi-sensor system. *Journal of Volcanology and Geothermal Research*, 143(4), 319–333. <https://doi.org/10.1016/j.jvolgeores.2004.12.004>
- Shinohara, H., Yoshikawa, S., & Miyabuchi, Y. (2010). Degassing of Aso Volcano, Japan through an acid crater lake: Differentiation of volcanic gas-hydrothermal fluids deduced from volcanic plume chemistry. *AGU Fall Meeting Abstracts*.
- Shinohara, H., Yoshikawa, S., & Miyabuchi, Y. (2015). Degassing activity of a volcanic crater lake: volcanic plume measurements at the Yudamari crater lake, Aso volcano, Japan. In *Volcanic Lakes*, (pp. 201–217). Springer. https://doi.org/10.1007/978-3-642-36833-2_8

- Sigurdsson, H., Carey, S. N., & Espindola, J. M. (1984). The 1982 eruptions of El Chichón volcano, Mexico: Stratigraphy of pyroclastic deposits. *Journal of Volcanology and Geothermal Research*, 23(1-2), 11–37. [https://doi.org/10.1016/0377-0273\(84\)90055-6](https://doi.org/10.1016/0377-0273(84)90055-6)
- Sigvaldason, G. E. (1979). Rifting, magmatic activity and interaction between acid and basic liquids. Nord Volcanol Inst Rep, 7903.
- Symonds, R. B., Gerlach, T. M., & Reed, M. H. (2001). Magmatic gas scrubbing: Implications for volcano monitoring. *Journal of Volcanology and Geothermal Research*, 108(1-4), 303–341. [https://doi.org/10.1016/s0377-0273\(00\)00292-4](https://doi.org/10.1016/s0377-0273(00)00292-4)
- System, W. (2012). *Portable Diffuse Flux Meter with LI-COR CO₂ Detector, Handbook*. Italy: West Systems srl.
- Tamburello, G., Agosto, M., Caselli, A., Tassi, F., Vaselli, O., Calabrese, S., et al. (2015). Intense magmatic degassing through the lake of Copahué volcano, 2013–2014. *Journal of Geophysical Research: Solid Earth*, 120(9), 6071–6084. <https://doi.org/10.1002/2015jb012160>
- Taran, Y., Fischer, T. P., Pokrovsky, B., Sano, Y., Armienta, M. A., & Macias, J. L. (1998). Geochemistry of the volcano-hydrothermal system of El Chichón volcano, Chiapas, Mexico. *Bulletin of Volcanology*, 59(6), 436–449. <https://doi.org/10.1007/s004450050202>
- Taran, Y., & Rouwet, D. (2008). Estimating thermal inflow to El Chichón crater lake using the energy-budget, chemical and isotope balance approaches. *Journal of Volcanology and Geothermal Research*, 175(4), 472–481. <https://doi.org/10.1016/j.jvolgeoes.2008.02.019>
- Taran, Y. A., & Peiffer, L. (2009). Hydrology, hydrochemistry and geothermal potential of El Chichón volcano-hydrothermal system, Mexico. *Geothermics*, 38(4), 370–378. <https://doi.org/10.1016/j.geothermics.2009.09.002>
- Tassi, F., Vaselli, O., Capaccioni, B., Macias, J. L., Nencetti, A., Montegrossi, G., & Magro, G. (2003). Chemical composition of fumarolic gases and spring discharges from El Chichón volcano, Mexico: Causes and implications of the changes detected over the period 1998–2000. *Journal of Volcanology and Geothermal Research*, 123(1-2), 105–121. [https://doi.org/10.1016/s0377-0273\(03\)00031-3](https://doi.org/10.1016/s0377-0273(03)00031-3)
- Varekamp, J. C. (2015). The chemical composition and evolution of volcanic lakes. In *Volcanic Lakes*, (pp. 93–123). Springer. https://doi.org/10.1007/978-3-642-36833-2_4
- Varekamp, J. C., Luhr, J. F., & Prestegard, K. L. (1984). The 1982 eruptions of El Chichón volcano (Chiapas, Mexico): Character of the eruptions, ash-fall deposits, and gasphase. *Journal of Volcanology and Geothermal Research*, 23(1-2), 39–68. [https://doi.org/10.1016/0377-0273\(84\)90056-8](https://doi.org/10.1016/0377-0273(84)90056-8)
- Varekamp, J. C., Pasternack, G. B., & Rowe, G. L. (2000). Volcanic lake systematics II. Chemical constraints. *Journal of Volcanology and Geothermal Research*, 97(1-4), 161–179. [https://doi.org/10.1016/s0377-0273\(99\)00182-1](https://doi.org/10.1016/s0377-0273(99)00182-1)
- Werner, C., Christenson, B. W., Hagerly, M., & Britten, K. (2006). Variability of volcanic gas emissions during a crater lake heating cycle at Ruapehu volcano, New Zealand. *Journal of Volcanology and Geothermal Research*, 154(3-4), 291–302. <https://doi.org/10.1016/j.jvolgeoes.2006.03.017>
- Wolery, T. J. (1992). EQ3NR, a Computer Program for geochemical aqueous speciation-solubility calculations: Theoretical manual, users guide, and related documentation (Version 7.0); Part 3. Tech. rep., Lawrence Livermore National Lab., CA (United States).