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Abstract	We here present the first chemical characterization of the volcanic gas plume issuing from the Santa Ana crater lake, a hyper-acidic crater lake (pH of − 0.2 to 2.5) in north-western El Salvador. Our results, obtained during regular surveys in 2017 and 2018 using a Multi-GAS instrument, demonstrate a hydrous gas composition (H_2O/SO_2 ratios from 32 to 205) and SO_2 as the main sulfur species (H_2S/SO_2 = 0.03–0.1). We also find that gas composition evolved during our investigated period, with the CO_2/SO_2 ratio decreasing by one order of magnitude from March 2017 (37.2 ± 9.7) to November 2018 (< 3). This compositional evolution toward more magmatic (SO_2-rich) compositions is interpreted in the context of the long-term evolution of the volcano following its 2005 and 2007 eruptions. We find that, in spite of reduced (background-level) seismicity, the magmatic gas supply into the lake was one order of magnitude higher in March 2017 (total volatile flux: 20,200–30,200 t/day) than in the following periods (total volatile flux: 900–10,167 t/day). We propose that the elevated magmatic/hydrothermal transport in March 2017, combined with a 15% reduction in precipitation, caused the volume of the lake to decrease, ultimately reducing its sulfur absorbing and scrubbing capacity, and hence causing the gas plume CO_2/SO_2 ratio to decrease. The recently observed increases in temperature, acidity, and salinity of the lake are consistent with this hypothesis. We conclude that the installation of a continuous, fully-automated Multi-GAS is highly desirable to monitor any future change in lake plume chemistry, and hence the level of degassing activity.

Keywords separated by ' - '	Santa Ana volcano - Crater lakes - Volcanic gas plumes - Multi-GAS - Gas scrubbing - CO_2/SO_2 ratio - Wet volcano
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Electronic supplementary material

Table S1
Summary of all derived (molar) gas ratios in the Santa Ana crater lake plume.

For each ratio, the correlation coefficient of the best-fit regression line is indicated (R^2). SO_2 MAX is the peak SO_2 concentration measured in each measurement inteval where a ratio was calculated. (XLS 65 kb)

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RESEARCH ARTICLE

The crater lake of Ilamatepec (Santa Ana) volcano, El Salvador: insights into lake gas composition and implications for monitoring

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Abstract

We here present the first chemical characterization of the volcanic gas plume issuing from the Santa Ana crater lake, a hyper-acidic crater lake (pH of − 0.2 to 2.5) in north-western El Salvador. Our results, obtained during regular surveys in 2017 and 2018 using a Multi-GAS instrument, demonstrate a hydrous gas composition (H_2O/SO_2 ratios from 32 to 205) and SO_2 as the main sulfur species (H_2S/SO_2 = 0.03–0.1). We also find that gas composition evolved during our investigated period, with the CO_2/SO_2 ratio decreasing by one order of magnitude from March 2017 (37.2 ± 9.7) to November 2018 (< 3). This compositional evolution toward more magmatic (SO_2-rich) compositions is interpreted in the context of the long-term evolution of the volcano following its 2005 and 2007 eruptions. We find that, in spite of reduced (background-level) seismicity, the magmatic gas supply into the lake was one order of magnitude higher in March 2017 (total volatile flux: 20,200–30,200 t/day) than in the following periods (total volatile flux: 900–10,167 t/day). We propose that the elevated magmatic/hydrothermal transport in March 2017, combined with a 15% reduction in precipitation, caused the volume of the lake to decrease, ultimately reducing its sulfur absorbing and scrubbing capacity, and hence causing the gas plume CO_2/SO_2 ratio to decrease. The recently observed increases in temperature, acidity, and salinity of the lake are consistent with this hypothesis. We conclude that the installation of a continuous, fully-automated Multi-GAS is highly desirable to monitor any future change in lake plume chemistry, and hence the level of degassing activity.

Keywords Santa Ana volcano · Crater lakes · Volcanic gas plumes · Multi-GAS · Gas scrubbing · CO_2/SO_2 ratio · Wet volcano

Introduction

The term wet volcano was introduced by Caudron et al. (2015) and is used to define a volcanic system characterized by the presence of an active voluminous magmatic-hydrothermal system. At such systems, the physical-chemical properties of crater lakes are key to volcanic activity monitoring (e.g., Rowe et al. 1992; Takano et al. 1994; Ohba et al. 2008; Christenson et al. 2010, 2015; Shinohara et al. 2015; Agusto and Varekamp 2016; de Moor et al. 2016a, 2019; Caudron et al. 2017). Temporal variations in the lake's physical-chemical state are thought to result from time-changing rates of heat and fluid supply from the underlying magmatic-hydrothermal system (e.g., Rowe et al. 1992; Christenson 2000; Ohba et al. 2008). However, Rouwet et al. (2016) has recently postulated that classic monitoring techniques, involving analysis of dissolved components in hyper-acidic crater lakes, are often of too low a temporal resolution to capture

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precursory signals to phreatic eruptions, the main hazard related to peak-activity crater lakes (e.g., Christenson et al. 2010; de Moor et al. 2016a, 2019). This observation has motivated further work to provide higher temporal resolution time series to track long- and short-term changes at crater lakes, to identify the parameters that need to be measured, and the processes they can be used to track.

The magmatic gas species usually monitored in fumaroles and plumes of open-vent volcanoes (Fischer and Chiodini 2015) can also be detected in the gas plumes released by hyper-acidic lakes. For hyper-acidic lake conditions, CO_2 is not absorbed into lake water, but SO_2 variably reacts with lake water to form H_2SO_4 (e.g., Tamburello et al. 2015; de Moor et al. 2016a, 2019; Gunawan et al. 2016), and HCl degassing accelerates if pH < 0 conditions are met (Capaccioni et al. 2017). The Multi-GAS instrument (Aiuppa et al. 2005a; Shinohara 2005), while traditionally used to monitor volcanic gas composition at "dry volcanoes" (e.g., Aiuppa et al. 2009, 2018; de Moor et al. 2016b), has recently proven to be useful in measuring gas plumes from crater lakes (Shinohara et al. 2015; Tamburello et al. 2015; Gunawan et al. 2016; Hasselle et al. 2018) and in detecting precursory changes to phreatic eruptions (de Moor et al. 2016a, 2019). High-frequency, continuous observations of gas compositions discharging from lakes can be of paramount importance in monitoring volcanic activity and in forecasting phreatic/phreatomagmatic eruptions (Stix and de Moor 2018; Battaglia et al. 2019).

Here, we characterize for the first time the composition of the lake gas plume released by Santa Ana crater lake (March 2017–November 2018). We interpret the temporal changes observed in tandem with lake level variations, SO_2 flux record, and seismicity, in an attempt to derive constrains on the current activity state and to speculate on the potential changes that might herald future reactivation of this restless volcano.

Geological and volcanological settings

Ilamatepec or Santa Ana volcano (13° 51′ N, 89° 37.5′ W; 2381 m asl) is located in western El Salvador (Fig. 1) and is surrounded by two highly populated cities, Santa Ana (pop. 522,000) and Sonsonate (pop. 420,000), both lying within a radius of 25 km from the volcano (Pullinger 1998; Colvin 2008). It is one of the most active volcanoes in El Salvador, with 13 VEI 2–3 eruptions reported since AD 1500 (Mooser et al. 1958; GVP 2018), mostly phreatic to phreatomagmatic in nature (Pullinger 1998). The last magmatic eruption occurred on October 1, 2005 (Scolamacchia et al. 2010) and was followed by small phreatic eruptions on March 15 and April 27, 2007. The youngest of the current four summit craters (0.5-km diameter) has hosted a small hyper-acidic crater lake (Bernard et al. 2004; Colvin 2008; Colvin et al. 2013) since 1904 (Carr and Pontier 1981).

The Santa Ana-Izalco-Coatepeque volcanic complex (< 200 ka; Pullinger 1998) includes two stratovolcanoes (Santa Ana and Izalco), the Coatepeque caldera (that is filled with a lake, Cabassi et al. 2019), and many parasitic cones, cinder cones, and explosion craters (Fig. 1; Pullinger 1998). The complex is part of the Central American Volcanic Arc, which results from subduction of the Cocos Plate below the Caribbean Plate (Carr 1984; DeMets et al. 1990).

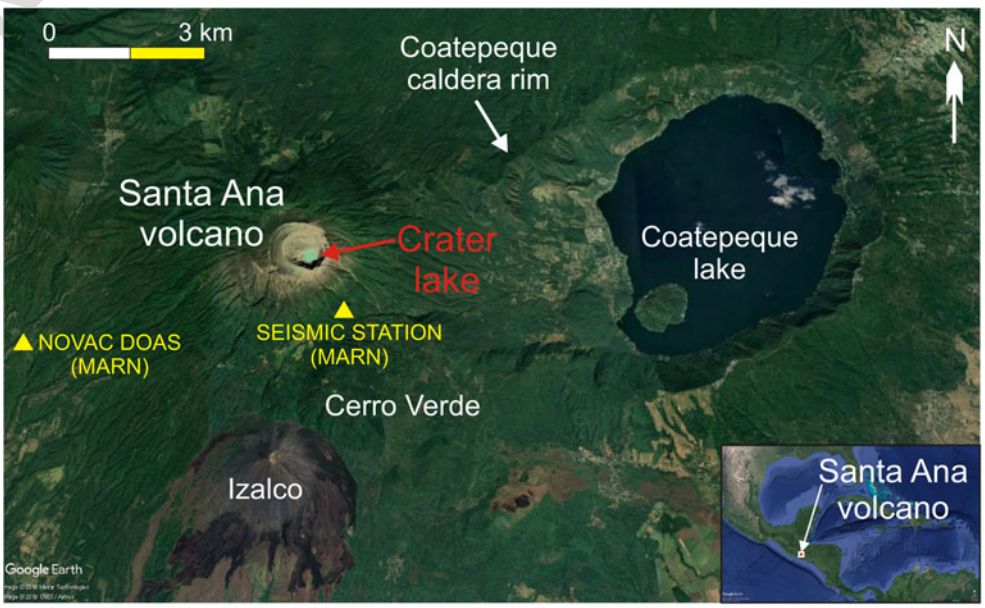

Fig. 1 Google Earth image (Image © 2019 Maxar Technologies) of the Santa Ana volcano and its surroundings. The location of the DOAS and seismic stations run by MARN are indicated. Inset: location of Santa Ana volcano in Central America

Temporal evolution of the crater lake

A large and permanent hydrothermal system beneath the volcano is implied by the many phreatic to phreatomagmatic eruptions of Santa Ana in the last thousand years (Pullinger 1998; Bernard et al. 2004). The hydrothermal system, topped by the hyper-acidic crater lake, manifests as hot springs along the lake shore, lake gas bubbling, and fumarolic emissions west of the lake. In 2000–2002, the lake floor was bowl-shaped, with a diameter of 200 m and a maximum depth of 27 m (Bernard et al. 2004). Along the shoreline, bubbling hot springs were observed (T~80 °C; Bernard et al. 2004). Prior to the October 2005 eruption, high-temperature fumaroles discharged vigorously although showing a marked temperature decline between 2002 and 2003 (being 532 °C in January 2000, 875 °C in June 2002, 264 °C in December 2003, 360 °C in January 2004; Bernard et al. 2004; Scolamacchia et al. 2010; SNET Monthly Report). The 2005 and 2007 eruptions drastically modified lake geometry, temperature, and water chemistry, possibly due to changes in rate and composition of the volcanic gas input (Colvin 2008; Colvin et al. 2013; Laiolo et al. 2017) (Fig. 2). The discharge rate and temperature of the fumaroles also decreased (to < 100 °C). However, the period 2010–2014 was poorly documented, inhibiting detailed evaluation of the activity of Santa Ana crater lake (Fig. 2).

Colvin (2008) proposed a physical model of the Santa Ana magmatic-hydrothermal system. According to Colvin (2008), a shallow degassing magma body (3–7 km depth, Carr and Pontier 1981; Halsor and Rose 1988) was overlain by a single-

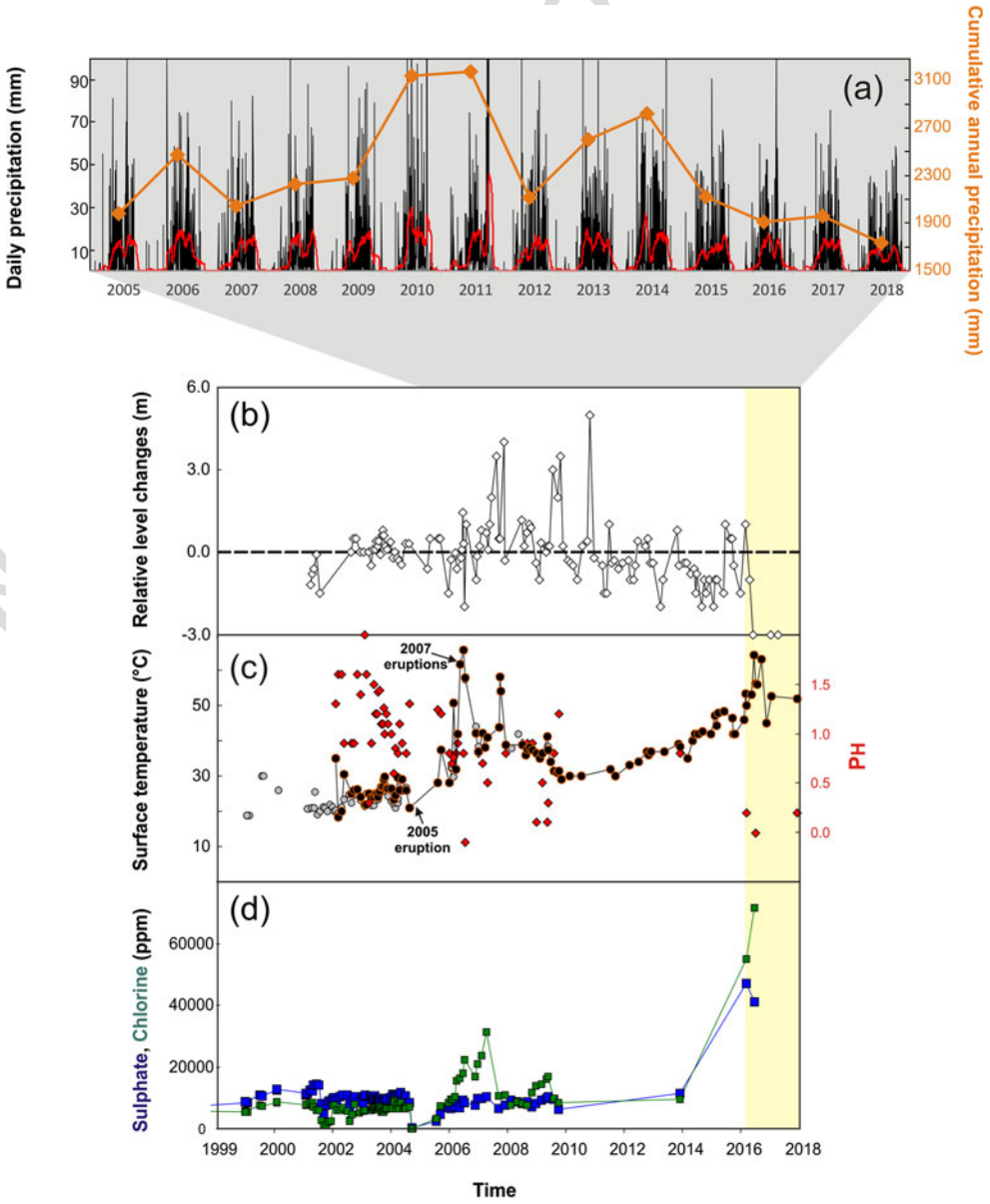

Fig. 2 Temporal variations in crater lake level, chemico-physical parameters and chemistry, 1999–2018 (the yellow-colored band identifies the temporal window covered by our Multi-GAS observations). **a** Daily precipitations (in mm) in the Santa Ana area (black line, left axis; the red solid line is a 30-day mobile average). The cumulative yearly precipitations. **b** Changes in lake level, in meters, expressed relative to a fixed benchmark position in the inner crater walls. **c** Temporal changes in lake surface temperature (left scale, gray circles, Bernard et al. 2004; Scolamacchia et al. 2010; black circles, MARN monitoring database) and pH (right scale; red diamonds). **d** Dissolved SO_4 and Cl concentrations in the lake water are also shown (orange diamonds, right y-scale). Data from MARN monitoring database

phase vapor zone and acid-sulfate-chloride hot springs (before the 2005 eruption; Bernard et al. 2004). This vapor zone would be separated from a shallower (near-surface) two-phase (liquid + gas) region by a low-permeability mineral seal (Pullinger 1998; Bernard et al. 2004). The fumarolic field, present since at least the 1950s (Meyer-Abich 1956; Bernard et al. 2004), was ruptured during the 2005 eruption (Colvin et al. 2013). After the eruption, this part of the crater was flooded but the presence of sub-lacustrine fumaroles is highlighted by strong bubbling driving a vigorous convection cell at the lake surface. This was still visible in 2018.

Periodical changes in activity are common in the recent history of Santa Ana crater lake. High activity levels were reported in 1920 and July 1992 (Gutiérrez and Escobar 1994; Bernard et al. 2004). More recently, low-level activity periods (January–May 2000 and February 2002–June 2004) alternated with high activity periods (May 2000–February 2002 and June 2004–August 2005) and finally culminated in eruption on October 1, 2005 (Colvin 2008). Before (October 2005–March 2007) and after (May 2007–December 2007) the March–April 2007 phreatic eruptions, Colvin (2008) reported a high level of activity.

The recent evolution of the lake system, illustrated in Fig. 2, is characterized thanks to monitoring results provided by MARN (Ministerio de Medio Ambiente e Recursos Naturales), the Salvadoran environmental and natural resources research office. MARN regularly monitors fumarole temperature, lake water temperature, and pH, as well as meteoric precipitation at the Los Naranjos station (approximately 3 km NNW of Santa Ana crater lake) (Fig. 2a). Variations in crater lake level (Fig. 2b) are also assessed by MARN comparing the lake level from photographs taken at several dates with the lake level on a scaled reference photograph. According to MARN database and previous literature information (see figure caption for details), the pH of the lake water (Fig. 2c) showed strong fluctuations, between 2 and 0.5, before the 2005 and 2007 eruptions; after the March–April 2007 phreatic eruptions, the lake water pH dropped to − 0.2, the lowest pH measured so far. A sudden temperature rise of 10 °C occurred prior to the 2007 eruptions (Fig. 2c). Afterwards, the lake level oscillated considerably, but mostly rose after the 2007 eruption and until 2010. By mid-2010, lake water temperature had returned to pre-phreatic lake temperatures of 28–32 °C. From 2011, two main periods of lake level drop were observed in 2014–2015 and in June 2017 to January 2018. Since February 2011, the lake water temperature started a steady increasing trend, with a peak temperature registered in June 2017, yet below the pre-phreatic eruptive temperature of 65.6 °C. The most recent pH values are near zero, among the highest on record. Sulfate and chloride concentrations in the crater lake water both peaked in 2017, at respectively 41,000–47,000 mg/L and 54,000–71,000 mg/L (Fig. 2d). No data on water chemistry are available for 2018.

Methods

We investigated the composition of gases emitted from the surface of Santa Ana crater lake. Gas compositions were measured in situ by Multi-GAS (multicomponent gas analyser system) (Aiuppa et al. 2005a; Shinohara 2005). We used a compact sensor unit containing a non-dispersive infrared (NDIR) spectrometer (for CO_2; range = 0–3000 ppm); three electrochemical gas sensors for H_2S (range = 0–100 ppm), SO_2 (range = 0–200 ppm), and H_2 (range = 0–200 ppm); and a relative humidity sensor (range = 0–100%) for indirectly measuring H_2O.

An explorative Multi-GAS survey was conducted at Santa Ana in March 2017 to investigate the composition of the lake gas plume for the first time. Measurements were obtained using a mobile Multi-GAS from three distinct sites in the crater area, located at different distances from the lake (Fig. 3): (i) on the S and SW outer crater rims, > 400 m from the lake; (ii) on the plateau, ~ 200 m NNE from the lake; and (iii) on the eastern lake shore. The same operations, at the same measurement sites, were repeated in June 2017, and a continuously recording Multi-GAS (measuring at 0.5 Hz rate in 4 daily measurement cycles of 30 min each) was run on the plateau site between June 5 and 13 (Fig. 3). Based on the results of these initial surveys, the plateau site (Fig. 3) was selected as the best location for deployment of a semi-permanent station, owing to relatively safe access compared to the lake shore and denser plume conditions compared to the outer rim. This semi-permanent station operated in April 2018 for 3 days, while punctual measurements for periods of ~ 2 to 3 h were also performed at the same site on May 3 and June 28, 2018. In November 2018, measurements were taken at both the plateau and the lake shore. Analytical data are summarized in Table S1. During the periods of observation, only a few low-temperature weakly degassing fumaroles (and a few hot springs) were visible, mostly on the SW shore and on the inner crater slope.

During our measurement period, both seismicity and SO_2 fluxes remained at background levels (Fig. 4), at least relative to records obtained during the 2005 eruptive unrest (Olmos et al. 2007). Seismicity was registered at the MARN seismic station located at San Blas, 1 km SE from the crater (Fig. 1). The SO_2 fluxes were measured with the permanent DOAS instrument of the NOVAC network (Galle et al. 2010), installed at 6 km SW from the crater (Fig. 1) and elaborated by the MARN monitoring service. During our specific Multi-GAS measurements in 2017–2018, the SO_2 flux varied from 41 and 329 t/day and was slightly higher in 2017 (mean 165 ± 140 t/day) than in 2018 (mean 144 ± 77 t/day) (Table 1). Considering the absence of high-temperature fumaroles during the studied period, we consider the degassing crater lake as the exclusive source of the SO_2 detected by the DOAS.

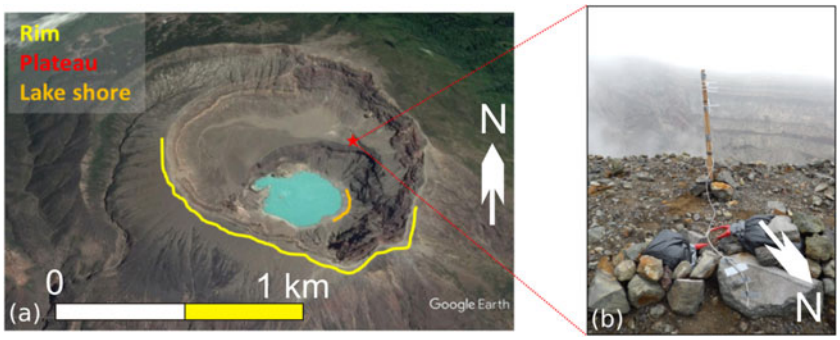

Fig. 3 **a** Google Earth image of Santa Ana volcano (Image © 2019 Maxar Technologies) with the location and tracks of Multi-GAS measurements in March 2017. The yellow and orange tracks correspond to measurements carried out by walking along the rim and the lake shore, respectively. The red star is the plateau measurement site. It is also the location where the **a** semi-permanent Multi-GAS was installed in June 2017 and in 2018 (**b**).

Results

Examples of Multi-GAS acquisitions at the three sites (rim, plateau, and lake shore), taken in the explorative March 2017 campaign, are given in Fig. 5. At the crater outer rim, in March and June 2017, we detected low amounts of SO_2 (~ 1 ppm) and H_2O (~ 1000s ppm above atmospheric background) (Fig. 5). H_2S concentrations were very low (~ 0.1–0.4 ppm) and poorly correlated with SO_2 peaks, and the volcanic plume was typically too diluted for a volcanic CO_2 signal to be resolved over the atmospheric background (Fig. 5a). At the plateau and the lake shore, all the target volcanic gases (CO_2, SO_2, H_2, and H_2O) were detectable in the plume at concentrations higher than 1 ppm (see examples shown in Fig. 5b, c). At the plateau, gas concentrations varied considerably over time. In the acquisition example of Fig. 5b, SO_2, CO_2, H_2, H_2O, and H_2S

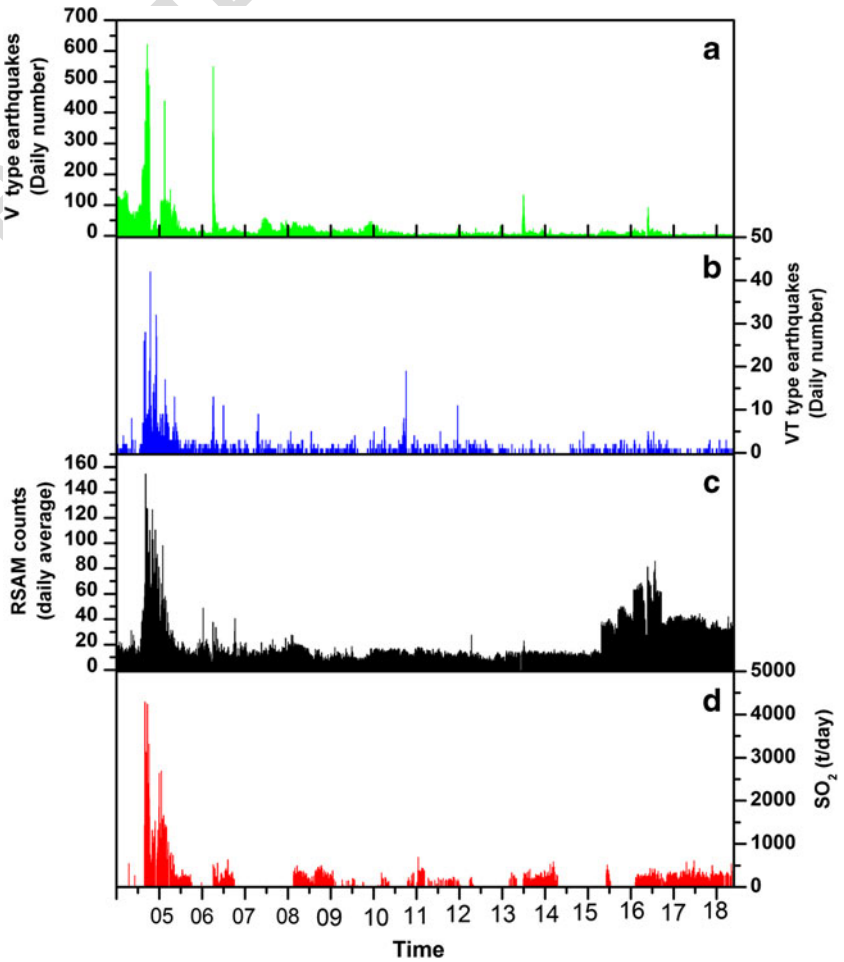

Fig. 4 2005–2018 time series of the seismic activity giving **a** number of volcanic events, V; **b** number of volcano-tectonic earthquakes, VT; **c** Real-time Seismic-Amplitude Measurement (RSAM); and **d** SO_2 flux at Santa Ana

t1.1 **Table 1** Daily averaged gas ratios (molar) at the plateau and lake shore, calculated by averaging all the ratios from Table S1 where peak SO_2 concentrations is higher than 7 ppm (filtered dataset). The gas fluxes (in tons/day) were calculated by scaling the daily mean gas ratios to the daily averaged SO_2 fluxes from the MARN DOAS station. 1σ is the standard deviation

t1.2	Date	Location	Peak SO_2	CO_2/SO_2	1 SD	H_2/SO_2	1 SD	H_2O/SO_2	1 SD	H_2S/SO_2	1 SD	SO_2 flux	1 SD	CO_2 flux	1 SD	H_2 flux	1 SD	H_2O flux	1 SD	H_2S flux	1 SD	TV flux	1 SD
t1.3	07/03/2017	Shore	16.5	31	13.7	0.42	0.11					240	96	5112	3049	3.1	1.5						
t1.4	07/03/2017	Plateau	8.2	37.2	9.7	2.39	0.27	205	14			240	96	6135	2931	18	7.5	13,825	5615			20,217	8649
t1.5	08/03/2017	Shore	26.6	54.5	24.9	0.54	0.06	190	11	0.03	0.01	329	132	12,320	7486	5.5	2.3	17,565	7106	5.2	2.7	30,225	14,728
t1.6	05/06/2017	Plateau	10.3	4.7	1.9	0.46	0.31			0.03	0.02	51	20	165	94	0.7	0.6			0.8	0.6		
t1.7	13/06/2017	Shore	20	5.4	0.1	0.06	0.02	77.4	3.9			41	16	152	61	0.1	0.04	892	360			1085	437
t1.8	13/06/2017	Plateau	15.6	4.2	1.4	0.84	0.75	75.8	48.2	0.06	0.03	41	16	118	62	1.1	1.1	873	657	1.3	0.8	1035	737
t1.9	06/04/2018	Plateau	14.7	4.1	1.6	0.52	0.57	177	11	0.08	0.02	87	35	245	137	1.4	1.6	4327	1753	3.7	1.7	4664	1928
t1.10	12/04/2018	Plateau	26.7	3.3	1.1	0.44	0.27	82	34	0.1	0.07	214	86	485	253	2.9	2.2	4931	2843	11	9.2	5644	3193
t1.11	13/04/2018	Plateau	24.8	3.2	0.7	0.39	0.17	62	37	0.08	0.07	61	24	134	61	0.7	0.4	1063	764	2.6	2.5	1261	853
t1.12	14/04/2018	Plateau	17.6	3.3	0.5	0.44	0.21	32	18			81	32	184	79	1.1	0.7	728	503			994	615
t1.13	03/05/2018	Plateau	29.5	2.9	0.8	0.39	0.15	75	26			117	47	233	113	1.4	0.8	2466	1306			2817	1467
t1.14	28/06/2018	Plateau	25.8	2.4	0.5	0.37	0.14	107	19			231	92	381	172	2.7	1.5	6945	3042			7560	3308
t1.15	28/11/2018	Shore	41.5	2.7	0.2			143	8	0.08	0.03	236	94	438	178			9483	3834	10	5.5	10,167	4112
t1.16	28/11/2018	Plateau	25	2.9	0.2	0.6	0.1	90	25			236	94	470	191	4.4	1.9	5968	2909			6679	3196

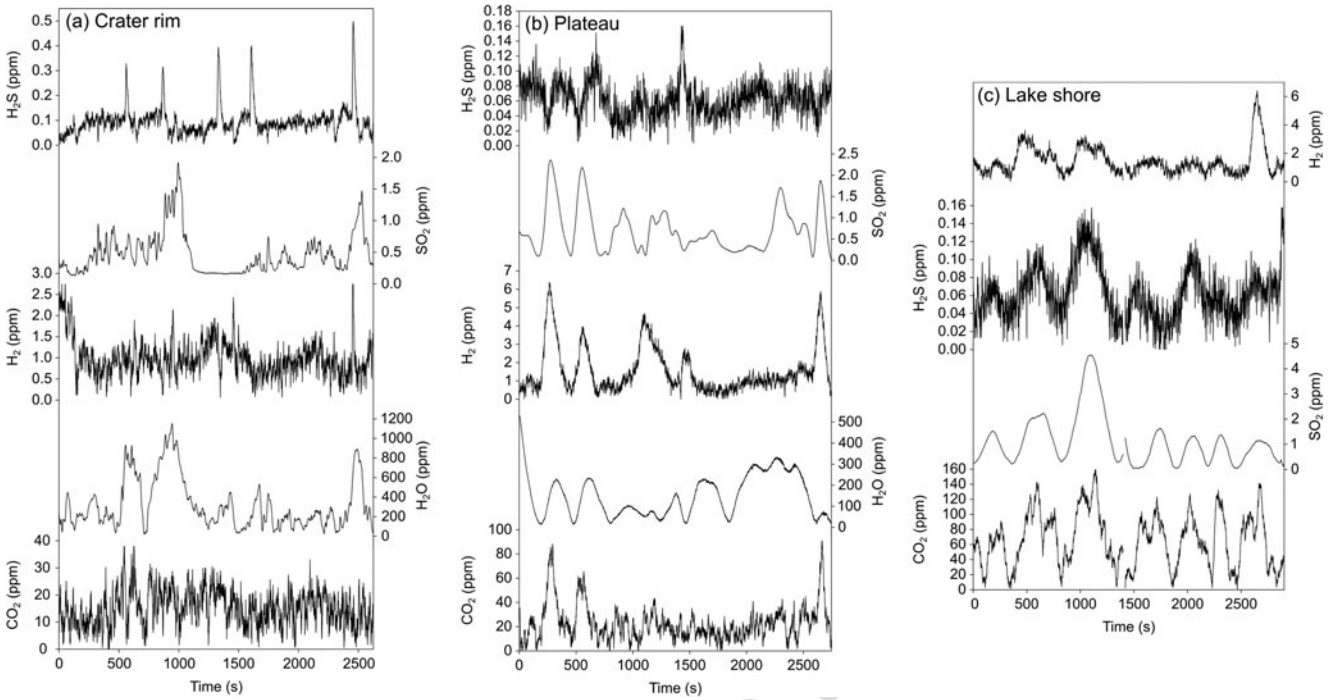

Fig. 5 Examples of Multi-GAS measurements at the crater rim (**a**), plateau (**b**), and lake shore (**c**) in March 2017

concentrations peaked at ~ 2.5, 80, 6, 300, and 0.14 ppm, respectively. Higher gas concentrations were observed episodically (in other acquisition windows), with peak concentrations of up to ~ 20 ppm for SO_2, ~ 150 ppm for CO_2 (above the atmospheric background of 403 ppm), ~ 20 ppm for H_2, ~ 3000 ppm for H_2O (above background), and ~ 1.3 ppm for H_2S (see Table S1). Measurements at the lake shore found the densest plume conditions (~ 30 ppm for SO_2) (Table S1). For practicality and safety reasons, the plateau site was selected for observations in 2018, except in November when the plateau and the lake shore were both accessed for measurement (Table S1).

The acquired concentration time series were processed using the scatter plot technique described by Hasselle et al. (2018). To do this, sequences of scatter plots (e.g., Fig. 6) were built for all sub-intervals where well-correlated concentration peaks were observed. Gas ratios were then obtained from the gradients of the best-fit regression lines. Gas ratios derived in this way are listed in the Appendix or Supplement (Table S1) and illustrated in the H_2/SO_2 vs. CO_2/SO_2 scatter plot of Fig. 7. The plot shows that both ratios span more than one order of magnitude and define a general compositional trend from SO_2-rich to H_2-CO_2-rich compositions. Our results also show that, even at the plateau location where a dense gas plume was detected, the obtained H_2/SO_2 ratios and, to a minor extent, the CO_2/SO_2 ratios were anti-correlated with SO_2 concentrations (Fig. 8), as observed elsewhere (e.g., at Masaya; Aiuppa et al. 2018). We cannot exclude that the high gas ratios at low SO_2 concentrations were (even partially) due to difficulties in resolving volcanic H_2 and CO_2 signals over the atmospheric backgrounds in dilute plume conditions—if so, the derived H_2/SO_2 and CO_2/SO_2 ratios would over-estimate the real volcanic signatures. Because of this possible concern, we find it more prudent to analyze the temporal trends in gas composition (Fig. 9) concentrating on the ratios obtained for sub-intervals with SO_2 above a 7-ppm concentration threshold where ratios become independent of SO_2 concentrations (Fig. 8). The daily averaged gas ratios derived from the filtered (> 7 ppmv SO_2) dataset are listed in Table 1.

Our filtered dataset highlights considerable changes in gas composition during the investigated period (Table 1 and Fig. 9). In March 2017, we were only able to obtain CO_2/SO_2 and H_2/SO_2 ratios at both the plateau and lake shore (Fig. 9 and Table 1). The daily averaged CO_2/SO_2 ratios were similarly high at both lake shore (31.0 ± 13.7) and plateau (37.2 ± 9.7).

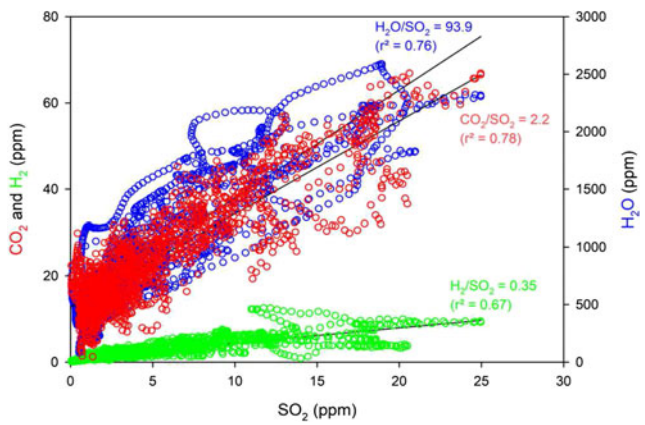

Fig. 6 Example of gas vs. SO_2 correlation plot in the form of a CO_2, H_2, H_2O vs. SO_2 scatter plot. Data taken at the plateau on June 28, 2018

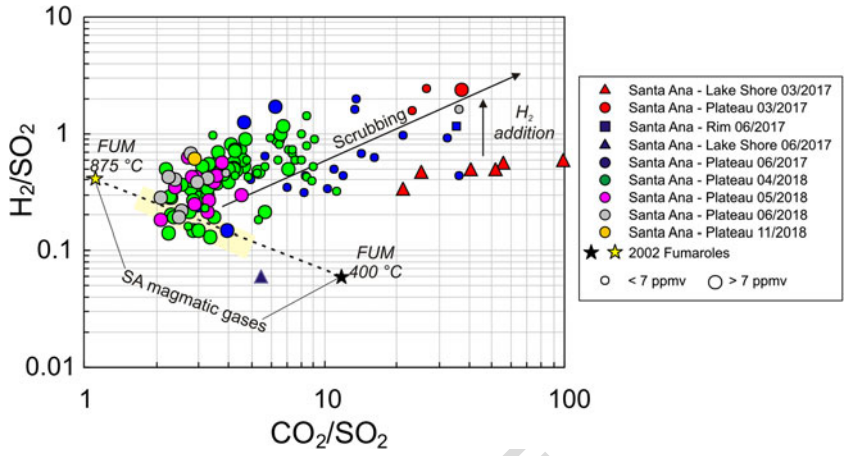

Fig. 7 H_2/SO_2 vs. CO_2/SO_2 ratios of Santa Ana lake gas emissions in 2017–2018 (data from Table S1). The compositions of high temperature fumaroles collected in June 2002 are also shown (sampled and analyzed by T.F.). From these, the yellow-colored area represents the inferred hypothetical composition of magmatic gases entering the Santa Ana crater lake in 2017–2018. FUM = fumarole as sampled by T.F.

The H_2/SO_2 ratios were 0.42 ± 0.11 at the lake shore and higher (2.39 ± 0.27) at the plateau. In June 2017, the CO_2/SO_2 ratios were drastically lower than in March (see Table 1), and again similar at both measurement sites (5.4 ± 0.1 at the lake shore and 4.2 ± 1.4 at the plateau; Fig. 9). The same contrast in H_2/SO_2 ratios (already seen in March) between lake shore (0.06 ± 0.02) and plateau (0.46 to 0.84 ± 0.75) was observed, but at both sites, a H_2-poorer (SO_2-richer) gas than in March was detected. The H_2S/SO_2 ratios were similar in March and June 2017 (0.03 to 0.06). The daily averaged H_2O/SO_2 ratios were of 190 to 205 in March 2017 and of 75.8 to 77.4 in June (Table 1).

A further decrease in CO_2/SO_2 ratios was observed at the plateau in April, May, June, and November 2018, when the daily averaged ratio ranged between 4.1 ± 1.6 (April) and 2.4 ± 0.5 (June) (Table 1; Fig. 9). The H_2/SO_2 ratios in May–June 2018 were also the lowest (daily averages from 0.37 ± 0.14 to 0.39 ± 0.15) observed at the plateau since observations started at Santa Ana (Fig. 7). In 2018, the gas composition remained H_2O-rich (H_2O/SO_2 between 32 ± 18 and 177 ± 11), and the H_2S/SO_2 ratio varied between 0.08 ± 0.07 and 0.1 ± 0.07 (Table 1). H_2S was below detection limit in May and June 2018.

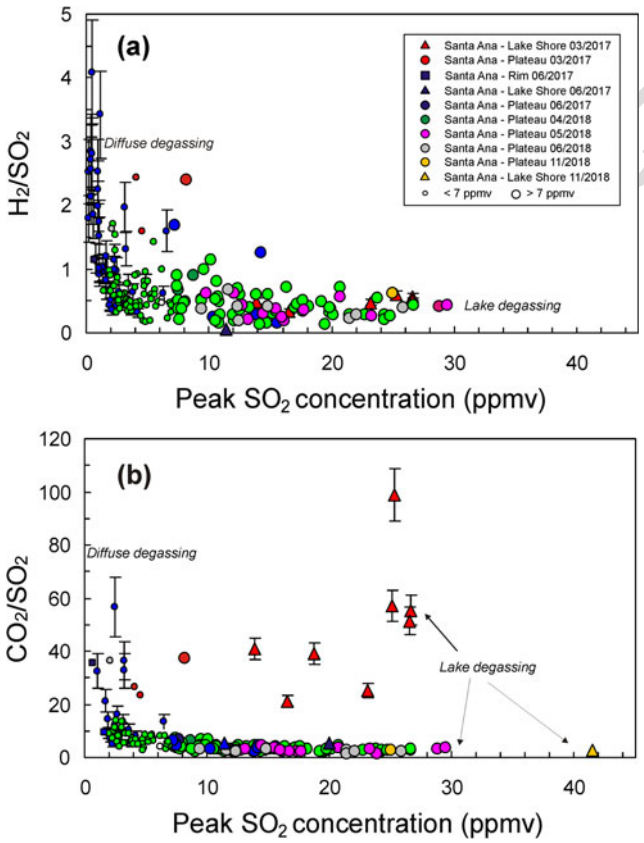

Fig. 8 Scatter plots of derived **a** H_2/SO_2 and **b** CO_2/SO_2 ratios vs. the peak SO_2 concentration in each integration interval (data from Table S1). At low (< 7 ppmv SO_2, small symbols) gas concentrations, the derived ratios are negatively correlated with SO_2 (taken as a proxy of plume density). At higher (> 7 ppm of SO_2, large symbols), gas ratios are independent on concentrations and are thus well representative of lake degassing only. The vertical error bars illustrate errors in the derived ratios (shown for a few selected data point only for clarity)

Discussion

The Santa Ana crater lake has frequently witnessed phreatic and phreatomagmatic eruptions in historical time, most recently in 2005 and 2007, and thus poses a potential threat to local inhabitants and numerous visitors. Colvin et al. (2013) suggested that the crater lake entered a new period of quiescence in early 2008, though with a higher steady-state mass/energy input than before the 2005–2007 eruptions. This quiescent phase was confirmed by the low levels of background seismicity and SO_2 fluxes (Fig. 4) and by the relatively stable lake temperature and chemistry (Fig. 2) (Colvin et al. 2013). The most recent data suggest, however, that a new cycle of lake surface temperature increase, and pH decrease, started sometime between late 2010 and early 2017 (Fig. 2). Although trends in lake water chemistry are difficult to interpret, due to the discontinuous nature of the dataset, sulfate and chloride concentrations were found to be

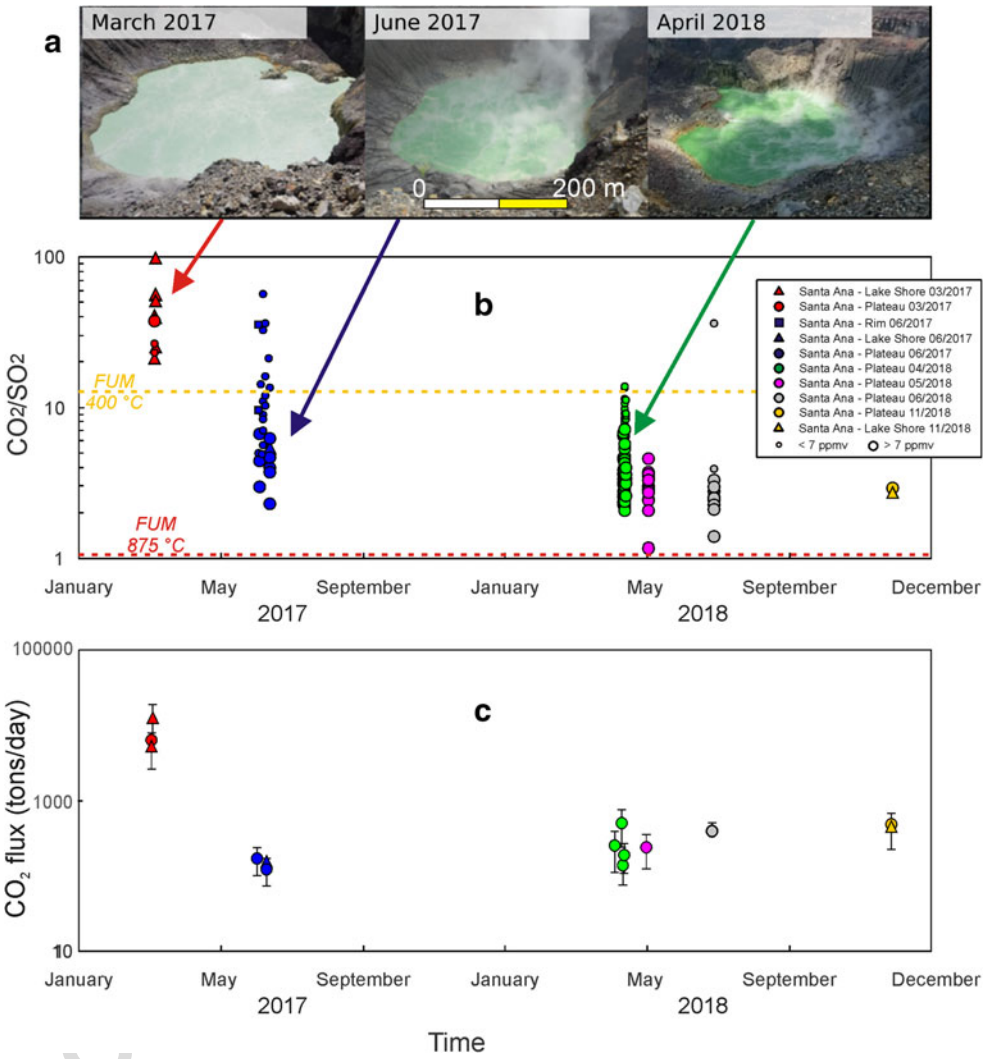

Fig. 9 Variations in **a** the lake level, **b** CO_2/SO_2 ratios, and **c** CO_2 fluxes, between March 2017 and June 2018 (data from Table S1 and Table 1). Dashed lines in **b** are the CO_2/SO_2 gas ratios of high-temperature fumaroles in 2002 (sampled by T.F.)

higher in 2014 than in 2010 and peaked in 2017 (Fig. 2). Overall, this evolution in lake water chemistry and temperature may potentially imply renewed unrest and therefore needs careful scrutiny.

Our lake gas plume results thus contribute to our understanding of the Santa Ana crater lake. Although the lack of similar data prior to 2017 (and especially prior to the 2005–2007 eruptions) partially hampers our interpretation, our gas data nevertheless contribute to assessing and hypothesizing on the current activity level at the crater lake. An important observation in this study is that the compositional features of the Santa Ana plume are heterogeneous, in both space and time.

Spatial variability

Measurements taken in 2017 from three distinct locations (rim, plateau, and shore), at different distances from the gas emission source (i.e., mainly the crater lake), imply some spatial heterogeneity in plume composition. At the rim, gas observations are complicated by the highly diluted nature of the plume detected; we consider the derived ratios strongly affected by analytical uncertainty, e.g., due to the difficulty in resolving volcanic gases over atmospheric background, especially for H_2O, CO_2, and H_2 (Fig. 5a). We hence conclude that the rim is not an ideal monitoring site, at least with the current state of activity at Santa Ana. The plateau, instead, is a far more promising monitoring site because, in addition to being safer and more accessible than the crater lake shore (Fig. 3), it is also systematically fumigated by a relatively dense plume (SO_2 at levels of tens of ppm). Importantly, our filtered dataset, in which measurements taken at higher plume density (SO_2 > 7 ppm) are considered (Table 1; Fig. 9), confirms that CO_2/SO_2 ratios exhibit overlapping ranges at plateau and shore in all campaigns (March and June 2017 and November 2018). The similarity of CO_2/SO_2 ratios (Fig. 10) at the plateau and shore confirms the utility of the latter site for monitoring. In contrast, H_2/SO_2 ratios at the plateau and at the shore do not match in both the March and June 2017 datasets, even in the filtered dataset (Table 1), and are systematically higher at the former, more distal site. We are confident that this

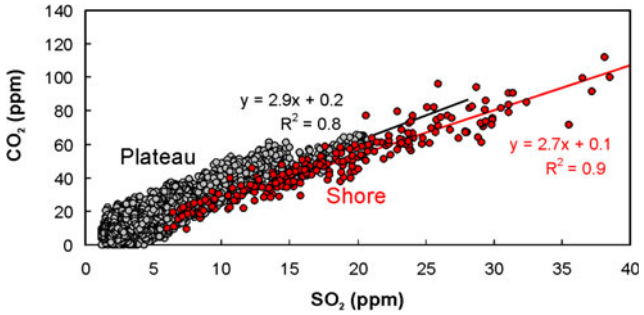

Fig. 10 CO_2 vs. SO_2 correlation plot for the simultaneous plateau (gray) and shore (red) Multi-GAS observations taken on November 28, 2018. The two derived CO_2/SO_2 ratios overlap within uncertainty

spatial change in composition (H_2/SO_2 ratio) cannot reflect analytical uncertainties, at least in the filtered dataset that includes only measurements taken in dense plume conditions, where ratios are independent of SO_2 concentrations (see Fig. 8). Also, SO_2 and H_2 are thought (Aiuppa et al. 2005b, 2011; Ehhalt and Rohrer 2009) to behave conservatively (i.e., to be poorly reactive) over the short travel times of seconds to tens of seconds associated with plume transport from the lake shore to the plateau. As such, we consider it unlikely that the H_2/SO_2 ratio difference between the shore and plateau is due to in-plume chemical processing. We find it, instead, more likely that the compositional change between plateau and shore reflect some additional H_2 contributions from other sources, perhaps weakly degassing hydrothermal fumaroles and steaming ground on the inner crater slope (Figs. 7 and 8). We suggest that these additional, diffuse gases (see Fig. 8) become mixed with the lake plume during plume transport between emission from the lake surface and measurement at the plateau, thus justifying the H_2 excess seen at the plateau (Figs. 7 and 8 and Table 1). This *diffuse degassing* source (see Fig. 8) may also explain the H_2-CO_2-enriched (relative to *lake degassing*; Fig. 8) compositions of dilute (SO_2 < 7 ppm) plateau and rim plumes.

Temporal trends

In addition to spatial heterogeneity, our measurements also highlight important temporal changes in gas composition (Fig. 9). We observed that the CO_2/SO_2 ratio decreased by more than one order of magnitude in 1 year, from March 2017 (shore 31.0 ± 13.7; plateau 37.2 ± 9.7) to June–November 2018 (< 3.0 at both shore and plateau) (Fig. 9). The H_2/SO_2 ratios at the plateau were also lower (and far less variable) in May–June 2018 than in March 2017, both in the total (Figs. 7 and 8) and filtered (Table 1) datasets. Overall, these observations imply a gas composition becoming more SO_2-rich over time. H_2S has remained a minor sulfur compound throughout the entire period of observation (Table 1).

In lake gas plumes, the S composition and flux reflect a complex and temporally variable balance between sulfur input flux into the lake via the magmatic/hydrothermal gas supply at the lake-bottom, gas scavenging by lake water as dissolved sulfur and/or mineral precipitates, and surface gas release (as either SO_2 or H_2S). Gas-water-rock reactions in the lake remove sulfur from the input gas via (Kusakabe et al. 2000; Christenson and Tassi 2015; Delmelle and Bernard 2015; de Moor et al. 2016a):

$$3SO2 + 2H2O \rightarrow 2HSO4^- + S(e) + 2H+ \quad (1)$$

$$4SO2 + 4H2O \rightarrow 3HSO4^- + H2S + 3H+ \quad (2)$$

$$2H2S + SO2 \rightarrow 3S(e) + 2H2O \quad (3)$$

in which S(e) is elemental sulfur. The increasingly SO_2-rich compositions of the Santa Ana lake plume gas in 2018, relative to 2017, suggest a shift of the above reactions toward the left, i.e., they indicate a lower consumption of the reagents during gas-water-rock reactions into the lake. A reduced SO_2 dissolution into the lake explains the tendency of our lake plume gas to become increasingly SO_2-rich (i.e., more magmatic in nature). The low H_2S contents in the Santa Ana lake plume imply that reaction mechanisms (1) and/or (2) are most likely involved because the reversal of reaction (3) should lead to H_2S formation, which is not observed.

The composition of the Santa Ana input gas in 2017–2018 is unknown, in view of the lack of measurable fumaroles. However, two high-temperature (400 to 875 °C) gas samples were collected at Santa Ana by one of us (T.F.) in June 2002. Assuming these compositions as representative of the current (2017–2018) magmatic gas input into the lake (Figs. 7 and 9) confirms that lake plume gas has become increasingly more magmatic in nature in 2018, relative to 2017. The triangular plots of Fig. 11 additionally support a progressive evolution of the Santa Ana plume gas toward more magmatic compositions. These plots compare the Santa Ana lake gas composition of this study with (i) the magmatic fumaroles in 2002 and (ii) the compositions of lake gas plumes recently obtained at other quiescent and/or recently active crater lakes worldwide (see caption for data sources). The plots confirm that, over the year of observations (2017–2018), the Santa Ana lake gas evolved in composition from CO_2-H_2-rich and S-poor to more S-rich, encompassing an intermediate position between the CO_2-H_2-H_2S-rich lake plumes as seen at "quiescent" crater lakes (e.g., El Chichón and Viti; Hasselle et al. 2018), and the far more SO_2-rich plumes issuing from "recently erupting" crater lakes (Yudamari, Copahue, Poás, and Rincón de la Vieja; Shinohara et al. 2015; Tamburello et al. 2015; de Moor et al. 2016a, 2019; Battaglia et al. 2019) (Fig. 11). The 2018 lake plume is also approaching the "magmatic" composition of the high-T (875 °C) fumarole sampled in the restless Santa Ana crater in 2002.

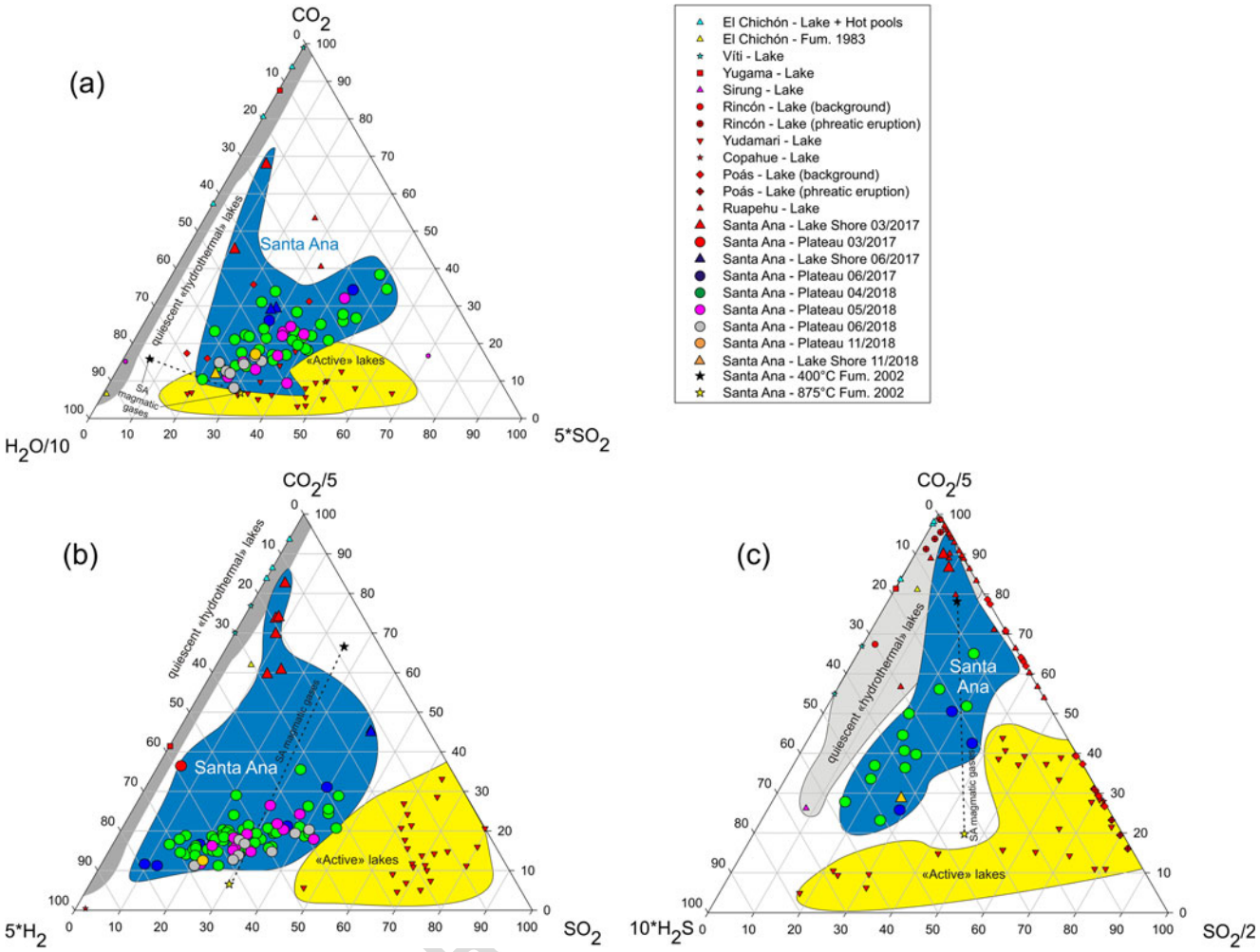

Fig. 11 Triangular plots (H_2O-CO_2-SO_2 (**a**), CO_2-H_2-SO_2 (**b**), and CO_2-H_2S-SO_2(**c**)) illustrating the temporal evolution of the chemical composition of the Santa Ana crater lake gas plume. The Santa Ana plume data (filtered dataset only; data from Table S1 filtered at the SO_2 threshold of ≥ 7 ppmv) are compared with a selection of crater lake plume compositions from El Chichón (Mexico; Hasselle et al. 2018), Viti (Iceland; Hasselle et al. 2018), Yugama (Kusatsu-Shirane volcano, Japan; Hasselle 2019), Yudamari (Aso volcano, Japan; Shinohara et al. 2015), Copahue (Argentina-Chile; Tamburello et al. 2015), Ruapehu (New Zealand; Hasselle 2019), Sirung (Bani et al. 2017), Poás (de Moor et al. 2016a), and Rincón de la Vieja (Battaglia et al. 2018). The 2018 Santa Ana plume gases have increasingly become more magmatic (more similar to the 2002 high-T fumaroles data of T.F.) with respect to the 2017 plume gases. Santa Ana crater lake gas occupies an intermediate position (blue-colored field) between "quiescent hydrothermal lakes" (El Chichón, Viti and Yugama; gray field) and "active lakes" (Copahue, Yudamari, Kawah Ijen; yellow field) Q9 Q10

Internal vs. external controls on lake gas evolution

The next obvious question is: what is the possible driver for the observed variations in gas compositions, and to what extent these signals represent potential hints for renewed volcanic unrest? SO_2 dissolution into volcanic crater lakes involves non-equilibrium, kinetically controlled gas-water-solid reactions (Kusakabe et al. 2000; Miyabuchi and Terada 2009; Christenson and Tassi 2015; de Moor et al. 2016a). Hence, since timing of gas-water interaction is the key factor, reduced sulfur absorption and scrubbing in 2018, as suggested by declining CO_2/SO_2 ratios, implies faster gas transit through the lake.

The gas transit time in a volcanic lake and, hence, the possible timescales of gas-water interactions scale to lake volume and depth (e.g., the deeper the lake, the longer the gas residence time) (Christenson and Tassi 2015) and input gas flux (de Moor et al. 2016a). Visual observations at the crater rim (Fig. 9) indicate that the Santa Ana crater lake level fell in 2018, relative to 2017. Our records (Fig. 2b) highlight that the crater lake level dropped by a maximum ~ 3 m between March and June 2017 and remained similarly low, or lower (Fig. 9), in April–May 2018. The dropping lake level in late 2017 to early 2018 is possibly part of a longer-term drying-out trend that started sometime in 2011 (Fig. 2b). Image-based, semi-quantitative estimates of relative lake level changes (Fig. 2b), based on relative level variations with respect to a reference level, show in fact that while the lake essentially rose in level from 2007 to 2010, the trend reversed since

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2011, when relative level changes have been either null (e.g., 2011–2013) or negative (e.g., 2015). The negative lake level fluctuations observed since June 2017 are, in particular, unique in the recent (post-2000) Santa Ana record and also correspond to a phase of peaking lake temperature, salinity, and acidity (Fig. 2c, d). As a result, we propose that the post-June 2017 reduced lake volume caused a general decrease in the gas residence time in the lake, leading to less efficient sulfur reactions with lake water and ultimately to more SO_2-rich lake gas plume compositions.

Precipitation records in the Santa Ana area (Fig. 2a) suggest that the recent decrease in crater lake volume may have been caused, at least partially, by a decreased meteoric water supply to the lake itself. Precipitation in the Santa Ana area nearly halved in 2018 relative to 2010–2011 and was ~ 15% lower than in 2017 (Fig. 2a). It is therefore likely that the reduced meteoric water influx contributed to reducing the crater lake volume. This conclusion is consistent with recent modelling work (Terada and Hashimoto 2017) demonstrating that low levels of precipitation can cause sizeable changes in crater lake temperature and composition, even at constant subaqueous gas input into the lake.

However, our gas flux measurements (Table 1) suggest that, in addition to reduced meteoric precipitations, an "internal" volcano-driven trigger was also likely at play. During our Multi-GAS surveys, the SO_2 fluxes were the highest in March 2017 (with daily averages of 240 and 329 t/day on March 7 and 8, respectively; see Table 1). By scaling our measured daily averaged lake plume gas ratios to the daily mean SO_2 fluxes, we can also calculate the H_2O, CO_2, H_2, and H_2S fluxes (Table 1). Results demonstrate that fluxes of H_2O (13,825–17,565 t/day), CO_2 (5117 to 12,320 t/day), and total volatiles (TV 20,217–30,225 t/day; the total volatile flux is the sum of H_2O + CO_2 + SO_2 + H_2 fluxes in our specific case) were one order of magnitude higher in March 2017 than at any time since (H_2O 892–9483; CO_2 118–485; TV 615–10167 t/day; Table 1). These results thus suggest that an increased gas supply from the sub-limnic magmatic-hydrothermal system (as implied by the anomalously high March 2017 fluxes) was a likely additional causal factor in driving the lake toward dryness. We propose that the elevated gas supply and, hence, heat transfer into the lake caused more intense lake evaporation (resulting in decreasing lake volume; Fig. 2b) and heating (where the lake warmed-up in late 2017; Fig 2c). We also argue that, because of the relatively high lake level in March 2017, the majority of the magmatic/hydrothermal S and Cl input was initially dissolved into the lake, thus justifying the anomalously elevated dissolved SO_4 and Cl (Fig. 2d) and the SO_2-poor lake plume gas (Fig. 9). In the following months, however, the lake level drop caused more rapid fluxing of gas through the lake, reducing the timescales of gas-water interactions and, thus, the lake's ability to scrub magmatic sulfur, ultimately determining a more magmatic (SO_2-rich) lake gas plume in late 2017 and in 2018. The lack of any sizeable change in seismicity (Fig. 4) perhaps suggests that the escalation in deep gas supply was not elevated enough to cause pressurization/fracturing of the sub-limnic hydrothermal-magmatic system.

Conclusions and implications for monitoring

Our novel gas plume results highlight the dynamic nature of the Santa Ana crater lake and reveal rapid compositional evolution in only 2 years of observation (2017–2018). However, available information on gas plume chemistry is too restricted in time to allow firm conclusions to be made on the current state of activity of the volcano. In particular, we cannot determine when the phase of elevated total volatile fluxes we observed in March 2017 actually started. Notwithstanding this, our results clearly show that the lake plume gas became increasingly more SO_2-rich, and therefore more magmatic in nature, in late 2017 and 2018. These gas variations have been paralleled by consistent variations in lake water chemistry and physical parameters, including increased lake temperature, acidity, and salinity, and a reduction in lake level and volume.

We propose these variations have been caused by a combination of external and internal processes, such as a decrease in precipitation and increased mass/heat supply at the lake bottom in March 2017, or before. In our interpretation, a ~ 15% drop in precipitation, and the elevated magmatic/hydrothermal fluid supply in March 2017, combined to reduce the lake volume. In turn, this resulted in a shortened magmatic gas transit time through the lake water. This lead to a reduction of magmatic sulfur reacting with lake water and ultimately to a more SO_2-rich gas plume.

The dynamic evolution of degassing at Santa Ana volcano, highlighted in the present study, argues for the need of further observations and careful scrutiny of water/gas compositional features in the very near future. Comparison with gas plume data from other crater lakes worldwide demonstrates that the 2018 Santa Ana lake gas is intermediate in composition between the CO_2-H_2-H_2S-rich lake plumes seen at "quiescent" crater lakes (e.g., El Chichón in Mexico), and the by-far more SO_2-rich plumes issuing from "recently erupting" lakes (e.g., Poás in Costa Rica). As such, any additional compositional change toward the SO_2-rich magmatic gas end-member should seriously be considered as evidence of activity escalation. At Laguna Caliente (Poás, Costa Rica), increasing SO_2 typically peaks prior to phreatic/phreato-magmatic eruptions (de Moor et al. 2016a, 2019; Stix and de Moor 2018), reflecting increasing magmatic gas influx into the lake. Although this critical situation seems not to have yet been reached at Santa Ana, our results underpin the need of reinforced volcano monitoring at this potentially hazardous volcano.

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