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- First volatile flux record of crater lake gas emissions from Copahue volcano
- Magmatic gases breaching through the lake surface
- Magmatic gas stripping drive enhanced lake water evaporation

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- Text S1 and Tables S1 and S2

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Intense magmatic degassing through the lake of Copahue volcano, 2013–2014

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Abstract Here we report on the first assessment of volatile fluxes from the hyperacid crater lake hosted within the summit crater of Copahue, a very active volcano on the Argentina-Chile border. Our observations were performed using a variety of in situ and remote sensing techniques during field campaigns in March 2013, when the crater hosted an active fumarole field, and in March 2014, when an acidic volcanic lake covered the fumarole field. In the latter campaign, we found that 566 to 1373 t d^{-1} of SO_2 were being emitted from the lake in a plume that appeared largely invisible. This, combined with our derived bulk plume composition, was converted into flux of other volcanic species ($H_2O \sim 10989$ t d^{-1}, $CO_2 \sim 638$ t d^{-1}, $HCl \sim 66$ t d^{-1}, $H_2 \sim 3.3$ t d^{-1}, and $HBr \sim 0.05$ t d^{-1}). These levels of degassing, comparable to those seen at many open-vent degassing arc volcanoes, were surprisingly high for a volcano hosting a crater lake. Copahue's unusual degassing regime was also confirmed by the chemical composition of the plume that, although issuing from a hot (65°C) lake, preserves a close-to-magmatic signature. EQ3/6 models of gas-water-rock interaction in the lake were able to match observed compositions and demonstrated that magmatic gases emitted to the atmosphere were virtually unaffected by scrubbing of soluble (S and Cl) species. Finally, the derived large H_2O flux (10,988 t d^{-1}) suggested a mechanism in which magmatic gas stripping drove enhanced lake water evaporation, a process likely common to many degassing volcanic lakes worldwide.

1. Introduction

Volcanic lakes that top the summits of active volcanoes result from complex interaction between volcanic/hydrothermal gases, surrounding rocks and meteoric waters [*Pasternack and Varekamp*, 1997; *Rouwet et al.*, 2015]. The dynamics of these interactions change radically in small or newly forming volcanic lakes, which are unstable systems prone to rapid changes in temperature and acidity, even for small gas inputs [e.g., *Werner et al.*, 2008]. During the first stages of a newly forming volcanic lake, water progressively enriches in solutes at a rate that is primarily controlled by the input fluxes of magmatic/hydrothermal vapors and by the rates of rock leaching. This process is countered by dilution due to meteoric recharge [*Brimhall and Chiorso*, 1983; *Kusakabe et al.*, 2000; *Symonds et al.*, 2001; *Varekamp et al.*, 2001]. Lake water heating is controlled by a balance between heat flux from the deep system, evaporation (the primary mechanism of energy dissipation), and addition of cold meteoric water [*Pasternack and Varekamp*, 1997]. If the water mass balance is net positive, the lake volume increases, together with the surface area as function of the shape of the crater. At this early stage, magmatic gases, such as SO_2, H_2S, HCl, and HF, are captured by the volcanic/meteoric water mixture [*Shinohara et al.*, 2015] generating a SO_4-Cl-rich acid brines with variable contents of solid or liquid sulfur [*Pasternack and Varekamp*, 1994; *Takano et al.*, 1994; *Varekamp et al.*, 2000]. Water/rock interaction causes the consumption of large amount of H^+ (through cation removal from rocks), leading to high dissolved contents of rock forming elements [*Varekamp et al.*, 2000; *Varekamp*, 2015] and trace elements [e.g., *Delmelle and Bernard*, 1994; *Henley*, 2015]. The water loss from evaporation increases together with the surface area of the lake, eventually tending to a steady state volume and temperature. Highly dynamic active crater lakes may even not reach a complete steady state [*Varekamp*, 2002] and undergo rapid volume variations (e.g., volume increase for a major rain event).

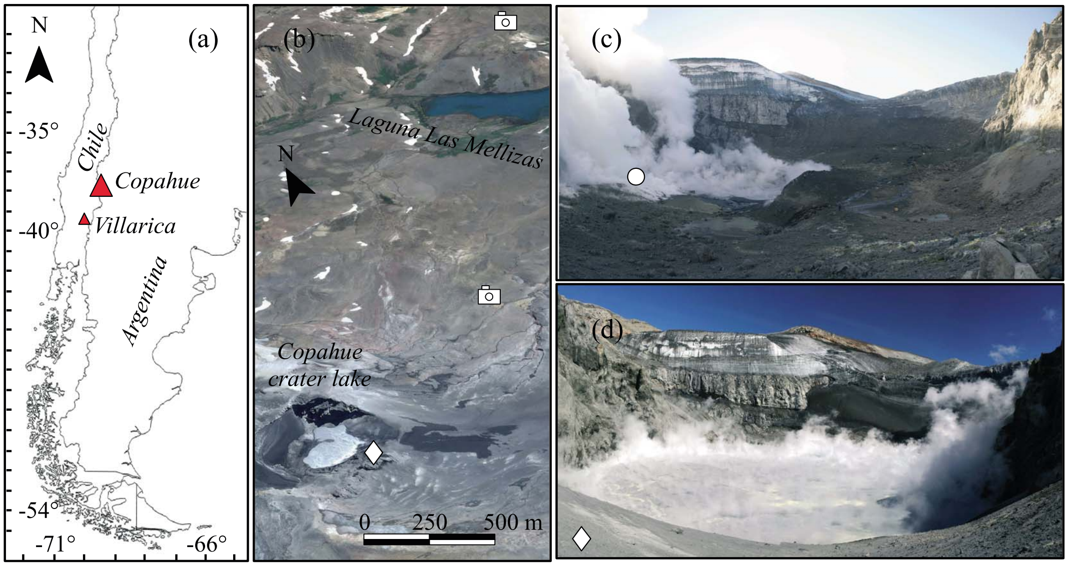

Figure 1. (a) Map of southern Argentina and Chile and positions of Copahue and Villarica volcanoes. (b) Copahue crater lake on 1 May 2014 seen from Google maps copyright satellite imagery and location of SO_2 camera measurement sites. (c) Copahue crater fumarolic field on 1 March 2013 and location of direct sampling site (white circle). (d) Copahue crater lake on 10 March 2014 and position of MultiGAS permanent measurements (white diamond).

As the pH at a crater lake becomes more acidic, scrubbing of the volcanic/hydrothermal gas stream becomes less efficient: at $pH < 3.8$, CO_2 is minimally absorbed by aqueous solution instead so that it can freely pass through the lake to be emitted to the atmosphere [*Pérez et al.*, 2011]; at $pH < 1$, chlorine is lost as a HCl-rich vapor [*Rouwet and Ohba*, 2015; B. Capaccioni et al., HCl degassing from extremely acidic crater lakes: empirical results from experimental determinations and implications for geochemical monitoring, submitted manuscript, 2015]. Gases escape from the lake surface as bubbles (convective/advective degassing) or by diffusion at the water/air interface [*Mazot and Taran*, 2009; *Caudron et al.*, 2012]. Diffusive lake CO_2 degassing has been measured in volcanic lakes worldwide using a floating accumulation chamber and infrared sensors [*Mazot et al.*, 2011, 2014; *Pérez et al.*, 2011]. These studies contributed a global volcanic lake CO_2 emission of ~94 Mt/yr or 4.2% of the global volcanic CO_2 fluxes [*Pérez et al.*, 2011].

The majority of the dynamic processes described above are presently active at Copahue volcano, which hosts a hyperacid lake formed by the interaction between magmatic/hydrothermal acidic gases and meteoric water from melting of the nearby glacier [*Varekamp et al.*, 2001]. The last eruptive cycle, started in July 2012 and still ongoing, alternated phreatic and phreatomagmatic events that caused disappearance of the lake in December 2012 and its progressive reestablishment after April 2013. This event provided a unique occasion to study the evolution of a newly forming crater lake toward an acidic end-member. The chemical composition of the lake was intensively studied over the past few years [*Varekamp et al.*, 2009; *Agusto et al.*, 2012], who recorded large preeruptive variations of major element ratios (e.g., Mg/Cl, Mg/K, and S/Cl) due to incipient dissolution of newly intruded magma into the acid hydrothermal reservoir. In contrast, no comparable information is available for volcanic gases issuing from the lake, and, although the hydrothermal gas discharges at the foot of Copahue volcano have been studied since 1997 by *Varekamp* [2008] and *Agusto et al.* [2013], the volcanic gas input is still largely unknown.

In this study we present the first observations of composition and emission rates of gas emissions from the Copahue volcano, obtained by combined in situ and remote sensing measurements carried out in 2013–2014. We use our novel data set to initialize quantitative models of the gas-water-rock interaction in the lake. These results contribute to refining our existing knowledge of volatile release from (and interaction within) hyperacidic water bodies.

2. Copahue Volcano

Copahue (37.856°S, 71.159°W) is an active stratovolcano in the central part of the Southern Volcanic Zone [*Stern*, 2004], located at the border between Argentina and Chile (Figure 1a). The volcano is situated on the rim of the large, ~2 Ma old Caviahue explosion caldera [*Bermúdez and Delpino*, 1995; *Varekamp et al.*, 2006]. During the last 250 years, 14 eruptions ranging in size from volcanic explosivity indexes 1–2 have occurred: in 1750, 1759, 1867, 1937, 1944, 1960, 1961, 1992, 1993, 1994, 1995, 2000, 2012, and 2014 [*Klohn*, 1946; *Moreno and Naranjo*, 1991; *Delpino and Bermúdez*, 1993; *Petit-Breuilh*, 1996; *Martini et al.*, 1997; *Naranjo and Polanco*, 2004]. Most eruptions were phreatic, with rare phreatomagmatic and sulfur pyroclastic emissions [*Delpino and Bermúdez*, 1993]. The volcanic edifice has an elliptical base (22 × 8 km) at 1650 m above sea level (asl), aligned in a SW-NE direction, and reaches a maximum elevation of about 2997 m asl. The eastern summit crater, which hosts a hyperacidic lake, is surrounded by walls of phreatic debris and glacier ice. Two acid hot springs (60–80°C), located at ~2500 m asl on the eastern flank [*Mangue*, 1978; *Martini et al.*, 1997; *Varekamp et al.*, 2001, 2004, 2009; *Caselli et al.*, 2005; *Agusto*, 2011], merge downstream to form the upper Agrio river (pH 2–3), which discharges into a large (~0.5 km^3) glacial lake (Lake Caviahue, pH ~3). Volcanic fluids are released into the lake from a magmatic-recharged hyperacid reservoir located in correspondence of the main volcanic conduit [*Varekamp et al.*, 2004]. Hydrothermal manifestations (boiling, bubbling, and mud pools) are located northeast of the volcano [*Mas et al.*, 1996, 2000; *Agusto et al.*, 2013] and derived from boiling of a hydrothermal reservoir, supplied by meteoric water and volcanic acid gases, with estimated temperatures of around 250–300°C [*Ouimette*, 2000; *Varekamp et al.*, 2004; *Agusto et al.*, 2013]. Geophysical measurements carried out in the framework of a geothermal exploration in this area [*Jurío*, 1977; *Panarello et al.*, 1988; *Sierra et al.*, 1992; *Mas et al.*, 2000] suggested the occurrence of two distinct hydrothermal reservoirs, located at 800–1000 m and 1400 m depth, respectively. Based on interferometric synthetic aperture radar data, the magma body which supplies the Caviahue-Copahue Volcanic Complex is likely located at ~5 km depth below the summit craters [*Velez et al.*, 2011].

In the last 3 years, besides the recurring eruptive events, the discharge rate of gases from the briny hyperacid lake ($pH < 0.5$) has significantly increased, as testified by recurrent reports by residents of Caviahue town (~3 km east of Copahue volcano) of persistent sulfur smell during windy days.

3. Material and Methods

Two sampling campaigns were carried out, in March 2013 and March 2014, respectively. During the first campaign, 3 months after the 2012 eruption, no acid crater lake was observed, permitting direct sampling of two fumaroles located at the bottom of the crater (Figure 1c). One year later (March 2014), the crater lake had reformed, being fed by a glacial meltwater waterfall from one side and characterized by milky white water with some fine floating sulfur. Despite the lack of evident bubbling activity in the lake, a steam plume rose diffusively from the lake surface, particularly from its southern edges. This volcanic gas plume and the lake water were analyzed during the last campaign.

3.1. Plume Measurements

We report here the first measurements of sulfur dioxide fluxes (SO_2) and the composition of gases (H_2O, CO_2, SO_2, HCl, HF, HBr, and H_2) in released from the Copahue crater lake. SO_2 fluxes were measured with a SO_2 camera system consisting of two JAI CM 140 GE cameras [*Kern et al.*, 2014]. Two UKA optics UV lenses (f 12 mm) were mounted to the fore of the cameras, providing a field of view of ~37°. Passband filters (Edmund Optics centered at 310 and 330 nm, 10 nm full width at half maximum) were placed behind each of these lenses, yielding reduced vignetting and lambda shift [*Kern et al.*, 2014]. Calibration was achieved with three quartz cells containing 98, 1030, and 2040 ppm m of SO_2, placed in front of the lenses. All the components were located inside a weatherproof box (30 × 20 × 15 cm), with an aperture sealed with a quartz glass UV transparent. The device was powered by an external 12 V, 7 Ah battery, its power consumption being <6 W.

On 6 and 10 March 2014, we deployed the SO_2 camera on the northeast flank of Copahue volcano, about 2300 m asl (Figure 1b). The site is ≈1.6 km from the crater (≈2760 m asl) and ensured a clear view of the plume moving toward the south-east with a speed of ≈10 m s^{-1}. Additional measurements were taken on 7 March 2014 at the more distal site of Laguna Las Mellizas (Figure 1b), ≈4.5 km from the crater, from which a clear view of a vertical buoyant plume in windless conditions was occasionally possible. Plume speed was evaluated with the integrated column amount (ICA) cross correlation method [*Tamburello et al.*, 2013] and ranged from 8–12 m s^{-1}.

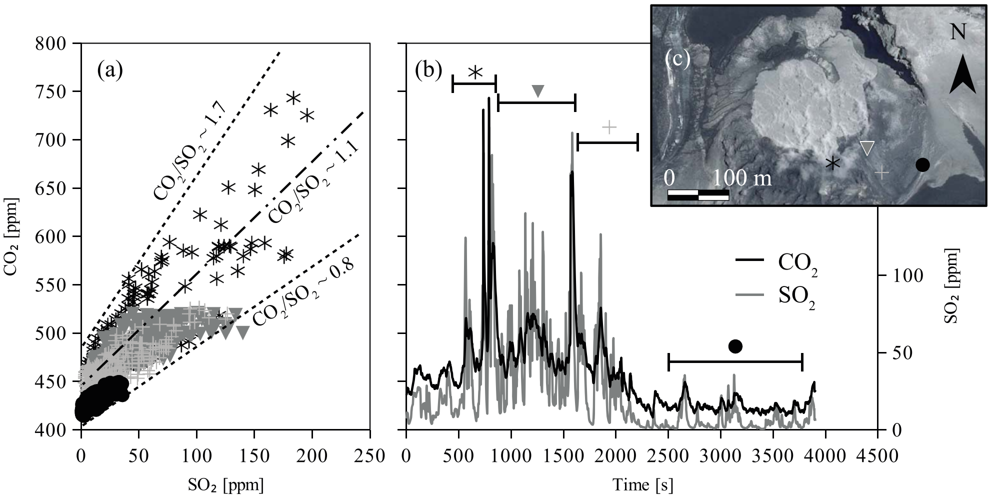

Figure 2. (a) Scatter diagram of CO_2 versus SO_2 concentrations time series (b) recorded during a survey close to the lake surface (black star, gray triangle, and gray cross) and on the rim (black circle). Black dashed lines in Figure 2a represents the minimum and maximum molar CO_2/SO_2 ratio measured by the permanent MultiGAS station located on the rim of Copahue. The dot-dashed line is the average CO_2/SO_2 molar ratio used as reference value in this work.

The composition of the gas phase issuing from the lake water surface was determined by a fully autonomous Multi-GAS analyzer that was temporarily installed on the crater rim approximately 100 m distance from the lake shore (Figure 1d). Signals from the H_2O, CO_2, SO_2, and H_2 gas sensors [see *Aiuppa et al.*, 2013] of the autonomous Multi-GAS were captured from a data logger board every 9 s during measurement cycles of 30 min each. From 6 to 10 of March, 30 cycles were performed, separated by repose intervals of 5 h. In order to investigate the chemical heterogeneity of the gas plume, an additional portable Multi-GAS was used for a survey along the lake shore and on the crater rim. Time series of H_2O, CO_2, SO_2, and H_2 concentrations, in parts per million by volume (Figure 2b), were collected with this portable device by placing the (tetrafluoroethylene) inlet probe 30 cm from the ground and walking from the lake surface to the rim of the crater. Halogens in the plume (SO_2, HCl, HF, and HBr) were in situ sampled by pumping air at a constant flow rate (4 L min^{-1}; sampling time, 10–60 min) through samplers consisting of three base-treated filters in series (filter packs), previously impregnated with 1 *M* $NaHCO_3$ [*Aiuppa et al.*, 2002, 2005]. All the samples collected were pretreated and preserved for their transport to the laboratory.

3.2. Direct Sampling

Fumarolic gases were collected in March 2013 from two vents located at the bottom of the summit crater (Figure 1c). Gases were collected using pre-evacuated 60 mL glass thorion-tapped flasks filled with 20 mL of a 4 N NaOH and 0.15 *M* $Cd(OH)_2$ suspension, according to the method proposed by *Montegrossi et al.* [2001] and analyzed at the laboratories of the University of Florence (Italy). Incondensable inorganic gases (N_2 and H_2) in the flask headspace were analyzed using a Shimadzu 15A gas chromatograph equipped with a 10 m long 5A molecular sieve column and a thermal conductivity detector (TCD). The alkaline suspension was used for determining the concentrations of (i) CO_2, as CO_3^{2-} by titration (Metrohm Basic Titrino) with a 0.5 N HCl solution; (ii) SO_2, as SO_4^{2-} after oxidation with H_2O_2; and (iii) HCl, as Cl^-, by ion chromatography (Metrohm IC 761). The solid precipitate was separated from the alkaline solution by centrifugation to determine H_2S by oxidizing CdS to SO_4^{2-} with H_2O_2 and then using ion chromatography. Hydrogen fluoride was analyzed as F^- in the condensate aliquot by ion chromatography.

3.3. EQ3/6 Models

The interaction between magmatic gases and the Copahue crater lake was numerically investigated using the EQ3/6 software package (7.0 version) [*Wolery*, 1979; *Daveler and Wolery*, 1992; *Wolery and Daveler*, 1992]. This program uses thermodynamic and kinetic constraints to simulate the reaction path of aqueous solutions that evolve through a set of irreversible (not at equilibrium) reactions toward a final equilibrium state [*Helgeson*, 1969]. Following *Marini and Gambardella* [2005], *Ilyinskaya et al.* [2015], and

Di Napoli et al. [2013], we simulated the effects of a scrubbing process [*Symonds et al.*, 2001] on the composition of water-soluble magmatic gas species due to interaction with an aqueous solution (the Copahue Lake, in our specific case, see Text S1 in the supporting information). The simulation was carried out considering a step-by-step addition of 300 mol of high-temperature magmatic gases (the initial gas) to 1 kg of an initial aqueous solution. Three distinct model runs were carried out, two at 65°C (to simulate magmatic gas scrubbing at shallow lake water conditions) and one at 300°C (to simulate magmatic gas scrubbing in the basal, hottest part of the lake, and/or at deep hydrothermal aquifer conditions) [*Ouimette*, 2000; *Varekamp et al.*, 2004]. Since the chemistry of the high-temperature magmatic gas supply underneath the lake is unknown [*Agusto et al.*, 2013], we used as initial gas (Table S1 in the supporting information) in EQ3/6 the composition of gases emitted by open-vent degassing at Villarica volcano [*Shinohara and Witter*, 2005]. This gas has been suggested [*Tamburello et al.*, 2014] as a representative proxy for the magmatic gas input in the southern volcanic zone of Chile and is here taken as representative of the deep gas (unaffected by scrubbing) feeding the activity of Copahue volcano. Additional tests were carried out by adding different amounts of gas (from 10 to 14,000 mol), yielding qualitatively similar model trends but less quantitative agreement with observations (natural gas data). The temperature of the initial gas (before interaction with the initial aqueous solution) was set at 1000°C, to account for some extent cooling from the initial magmatic temperature ($>$1000°C) [*Witter et al.*, 2004]. The runs were initialized using two distinct initial aqueous solutions. One run (CGWR_65°C) used as starting solution the chemical composition of a cold ($T = 4.1$°C), neutral (pH = 7.7), and low salinity (total dissolved solids, TDS = 300 mg/l) water (initial aqueous solution_1 in Table S1 in the supporting information) [*Holm et al.*, 2010] which we considered as representative of meteoric input into the Copahue Lake. This run was therefore representative of the formation of the lake, after prolonged interaction between meltwater recharges and magmatic gases. Two additional runs (CGLR_65°C and CGLR_300°C) used as initial aqueous solution are our measured composition of the Copahue Lake (initial aqueous solution_2 in Table S1 in the supporting information); these runs were therefore an attempt to simulate scrubbing of magmatic gases at the 2014-day lake conditions. In all simulations, a basaltic andesite was left free to dissolve as solid reactant into the lake during gas-water interaction. We used the averaged chemical compositions (see Table S1 in the supporting information) of *Naranjo and Polanco* [2004] and *Varekamp et al.* [2006] for Copahue basaltic andesites (SiAl0.36 Fe0.12 Mg0.13Ca0.14 Na0.13 K0.03 O3.02).

The output of each model run was the evolution of the model aqueous solution as a function of the advancement degree of gas-water-rock interaction process (as expressed by the reaction progress variable, ξ). In addition, at the end of each simulation run, the equilibrium total gas pressure ($P_{g,TOT}$) in the end-of-run aqueous solution was calculated by summing up the partial pressures of each gas species (taken from the EQ6 output files). Gas overpressuring ($P_{g,TOT} > P_{run}$) was observed in all four cases. We therefore calculated the chemical composition (n_j/nH_2O_g, where j is either CO_2, SO_2, H_2S, or HCl) of the gas phase released by single-step degassing of the end-of-run aqueous solution (for details on the procedure, see *Marini and Gambardella* [2005]), according to the relation

$$\left(n_j/nH_2O\right)_o = \left(n_j/nH_2O\right)_g \cdot f + \left(n_j/nH_2O\right)_l \cdot (1 - f) \tag{1}$$

where $(n_j/nH_2O)_o$ stands for the initial gas composition of each oversaturated, end-of-run aqueous solution (all extracted from the EQ6 output files), f is the fraction of separated gas, which was varied from $f = 0$ (e.g., no degassing) until $P_{g,TOT}$ in the residual (degassed) aqueous solution decreased to P_{run}. These model-separated gases ultimately represented the gas phases at equilibrium with the end-of-run aqueous solutions.

4. Results

4.1. Gas Composition

Two gas samples were directly sampled on 1 March 2013 from the fumarolic field located inside the Copahue crater (Figure 1c). The temperatures of the sampled gas were 102 and 431°C, respectively. The chemical composition of the dry gas fraction, expressed in millimoles per mole, and the molar percentage of water vapor in the gas discharges are reported in Table 1a. Dry gases were dominated by CO_2 (up to 7.06 mol %) and showed relatively high concentrations of acidic compounds, such as SO_2 (up to 1.57 mol %), HCl (up to $4.85 \cdot 10^{-2}$ mol %), H_2S (up to $8.29 \cdot 10^{-2}$ mol %), HF ($2.76 \cdot 10^{-2}$ mol %), and concentrations of H_2 (up to $8.67 \cdot 10^{-1}$ mol %). Unfortunately, the largest, hottest (estimated temperature of ~700°C) fumarolic vents, which contributed the

Table 1a. Outlet Temperature (in °C), Chemical Composition of the Dry Gas Fraction (in mmol/mol), and Steam Concentrations (in %) of Two Fumaroles of the Fumarolic Field of Dry Copahue Crater[a]

Date	*T* (°C)	CO_2	HF	HCl	SO_2	H_2S	N_2	H_2	O_2	H_2O
01/03/2013	431	7.05	$2.76 \cdot 10^{-2}$	$4.86 \cdot 10^{-2}$	1.57	$8.29 \cdot 10^{-2}$	$1.52 \cdot 10^{-1}$	$8.67 \cdot 10^{-1}$	$5 \cdot 10^{-3}$	90.2
01/03/2013	102	5.12	$1.62 \cdot 10^{-2}$	$2.37 \cdot 10^{-2}$	$7.5 \cdot 10^{-1}$	$5.56 \cdot 10^{-2}$	$8.74 \cdot 10^{-2}$	$3.5 \cdot 10^{-2}$	$8 \cdot 10^{-3}$	93.6

[a] Dates are formatted as day/month/year.

majority of the visible plume in 2013 (Figure 1c), were not accessible to sampling. The negative temperature dependence commonly exhibited by volcanic gas CO_2/SO_2 ratios [*Aiuppa et al.*, 2012, 2014] suggests for the latter fumaroles a lower CO_2/SO_2 ratio signature than observed in the two sampled, colder fumaroles ($CO_2/S_{tot} \sim 4.3$ and ~ 6.4).

During the March 2014 campaign, an acidic volcanic lake completely covered the fumarolic field, preventing direct sampling of gas vents. A Multi-GAS survey was therefore carried out (on 6 March) around the crater lake shore to investigate the composition of the gas/steam issuing from the lake surface. Despite variations in gas mixing ratios were observed at the different measurement sites (Figure 2c), the molar ratios between gas species (as constrained by scatter plots as in Figure 2b) were remarkably stable (e.g., CO_2/SO_2 1.1 ± 0.3, Figure 2a). In the same day, a fully autonomous Multi-GAS was installed on the highest point of the southern rim (Figure 2c, black circle), acquiring every 5 h at 0.11 Hz rate for half hour. Our 5 daylong Multi-GAS time series resulted in a constant bulk plume composition (H_2O/SO_2 41 ± 14.7, CO_2/SO_2 1 ± 0.3, SO_2/H_2 0.11 ± 0.05, 1σ, Table 1b and Figure 3), similar to that observed by the mobile (survey) Multi-GAS (Figure 2). H_2S was below the detection limit (<0.1 ppm) in both mobile and fixed Multi-GAS observations, demonstrating a plume H_2S/SO_2 ratio $< 10^{-3}$ (versus $H_2S/SO_2 \sim 0.06$ in 2013 fumaroles). A set (three) of filter packs was additionally collected on 6 and 10 March 2014 in the crater rim (Figure 1c) to characterize the halogen contents (Cl and Br) in the plume issuing from the lake plume (Table 1b). These yielded HCl/SO_2 and HBr/SO_2 ratios of ~0.12 and $\sim 4.5 \cdot 10^{-5}$, respectively. The distinct HCl/SO_2 ratios in 2013 (~0.03) and 2014 (~0.12) were likely related to a potentially larger effect of secondary processes (e.g., scrubbing), which affected the first sampling.

4.2. Gas Fluxes

The UV camera detected very high SO_2 column densities during the 2014 campaign (up to 2000 ppm m, Figure 4a) in a plume that was "invisible" in the visible region of the electromagnetic spectrum (Figure 4b) [e.g., *Werner et al.*, 2012]. The calculated SO_2 fluxes varied during each day as well as between the days and the momentary flux for single frame ranged between < 100 and $2900\ t\ d^{-1}$, mainly due to turbulence in the plume. Average daily fluxes for the 3 days were $928 \pm 386\ t\ d^{-1}$, $1{,}373 \pm 565\ t\ d^{-1}$, and $566 \pm 393\ t\ d^{-1}$ (Figure 4c), respectively, which gives a mean for the 3 days of $\sim 956\ t\ d^{-1}$, taken as typical value for Copahue during this interval.

4.3. Lake Composition

The presence of a crater lake has been a constant feature of the recent Copahue history [*Varekamp*, 2008]. Its persistence is mainly due to the continuous input from the melting glacier (~2800 m asl) to a well-sealed

Table 1b. MultiGAS and Filter Pack-Derived Molar Ratios[a]

Time	CO_2/SO_2	H_2O/SO_2	SO_2/H_2	HCl/SO_2	HBr/SO_2
06/03/14 22:55	0.96	31.8	0.157	0.093	$8.39 \cdot 10^{-5}$
07/03/14 03:56	0.91	17.4	0.045	0.097	$2.94 \cdot 10^{-5}$
07/03/14 08:58	1.49	26.2	0.12	NA	NA
07/03/14 14:10	1.05	37.4	0.098	NA	NA
07/03/14 18:52	0.73	40.98	0.073	NA	NA
07/03/14 23:47	1.02	48.9	0.1	NA	NA
08/03/14 00:07	0.69	47.3	0.1	NA	NA
08/03/14 04:50	0.75	64.7	0.09	NA	NA
08/03/14 14:49	1.09	57.3	0.197	NA	NA
10/03/14 12:08	0.93	29.6	0.058	0.1472	$2.04 \cdot 10^{-5}$
Average	0.97	40.87	0.11	0.12	$4.46 \cdot 10^{-5}$
Error (1σ)	0.3	14.7	0.046	0.03	$3.44 \cdot 10^{-5}$

[a] NA, not assigned. Dates are formatted as day/month/year.

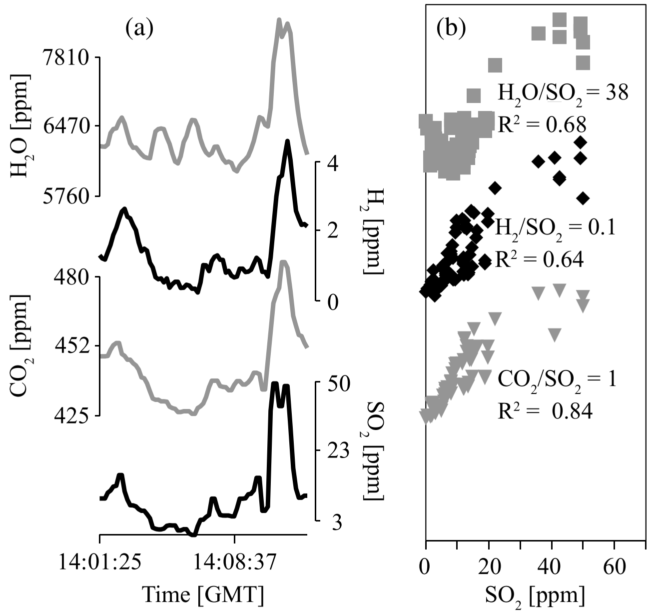

Figure 3. (a) Time series of H_2O, H_2, CO_2, and SO_2 concentrations measured on Copahue crater rim on 7 March 2014 and (b) scatter diagram of gas versus SO_2 which gas/SO_2 molar ratios are calculated from the gradient of the best fit regression lines.

bottom crater, whose permeability seems not to have been compromised by the numerous eruptions. On 10 March 2014, we sampled the water of Copahue crater lake from the accessible eastern rim (Figure 1d). At the time of the sampling, the lake exhibited a whitish color with clouds of steam rising from the surface and clusters of floating elemental sulfur. Our collected water sample shows a very low pH (0–1) and high contents of rock forming elements (RFE, up to 3102 mg l^{-1} of Mg^{2+}) and volcanogenic elements (halogens up to ~13,100 mg l^{-1} of Cl^- and sulfur ~17,200 mg l^{-1} of SO_4^{2-}) (Table 1c). This acid Cl-SO_4 brine composition reflects a continuous supply of volcanic gas and RFE elements acquired through water-rock interaction.

4.4. Model Simulations of Magmatic Gas-Lake Water Interactions

Figures 5 and 6 illustrate the results of the EQ3/6 simulations. The evolution of model aqueous solutions upon reaction path advancement (i.e., upon increasing values of the reaction progress variable, ξ) of the three model runs is shown along with the chemical compositions of natural samples in Figure 5 (Copahue Lake, this work, and *Varekamp et al.* [2009]). The model trend CGWR_65°C (see Table S2 in the supporting information) is representative of the model evolution of a dilute, meteoric water (representative of the meltwater recharge to the lake), after the injection of (and the interaction with) 300 mol of initial gas. It may represent the first stages of reestablishment of the crater lake after an eruption. As reaction progresses (e.g., with increasing ξ values), the model solutions become progressively more acidic (from pH = 7.7 down to pH ~0.5) and enriched in anions (Cl^-, F^-, and S_{TOT}) and cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}), reflecting the increasing extents of magmatic gas and rock dissolution. Upon advancement of the reaction path, the buffering role of solid reactant increasingly comes to play, leading to a slight pH increase (to pH ~1). A minor decrease of dissolved S_{TOT} is also observed, as due to S precipitation as native S, pyrite, and anhydrite from model solutions at lake temperature. Alunite would get saturated inside the hydrothermal system, at 250–300°C, as it did during earlier eruption and intrusions. Overall, a fair agreement is observed between

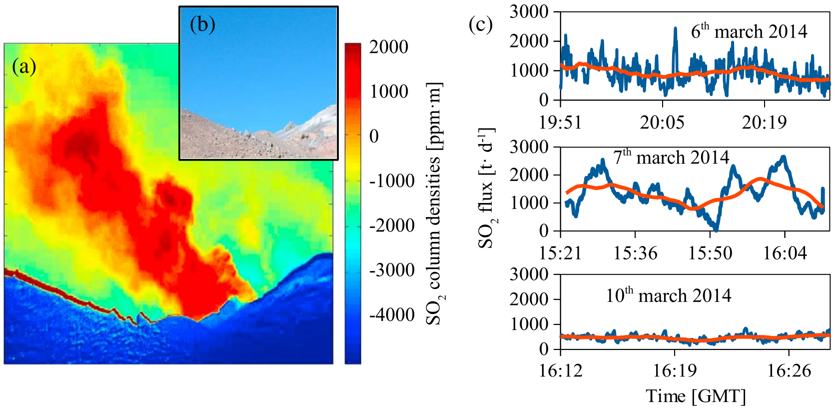

Figure 4. (a) SO_2 column densities measured at Copahue volcano with an SO_2 camera system from the foot of the volcanic edifice and (b) visible image taken from the same position. (c) Measured SO_2 flux time series.

Table 1c. Temperature and Chemical Composition of the Sampled Copahue Crater Lake[a]

Date	*T* (°C)	pH	F^-	Cl^-	Br^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^{2+}	K^+	NH_4^+	Li^+
10/03/2014	63	<0.5	1133	13082	82.4	17163	1129	3102	1284	233	3.95	4.95

[a] Date is formatted as day/month/year.

the CGWR_65°C (see Table S2 in the supporting information) model curve and the compositional trend exhibited by natural (lake water) samples (Figure 5). The end-of-run (CGWR_65°C) model solution has composition that agrees well (Cl^-, F^-, and S_{TOT}), or at least reasonably well (Na^+, K^+, and Ca^{2+}), with the Copahue Lake composition measured in February 2014. Model-predicted Mg contents are less consistent with observations. The three simulations carried out using the Copahue Lake composition as that of the initial aqueous solution (CGLR_65°C and CGLR_300°C) yield to somewhat overlapping trends (Figure 5). Importantly, these model trends exhibit only minor net increases in Cl^-, F^-, and S_{TOT} contents, relative to initial aqueous solution, supporting a reduced gas scrubbing efficiency of the Copahue Lake, compared to that of meteoric fluids (compare with the CGWR_65°C trend). Our models also confirm that rock dissolution is amplified with increasing temperatures (compare the model trends for rock-forming major cations at 65°C and 300°C).

Figure 6 compares the compositions of the model-separated gases (i.e., the gas phases separated at equilibrium, during single-step degassing of the end-of-run model aqueous solutions of Figure 5; cf. section 3.3)

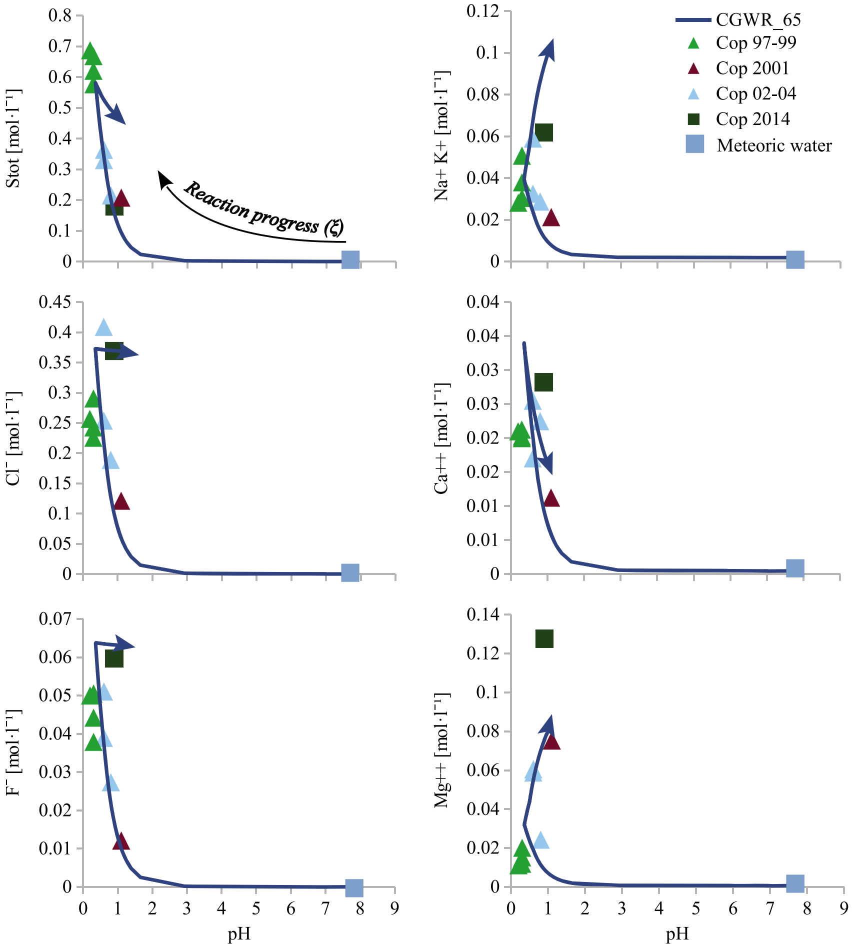

Figure 5. Evolution of the chemical composition of the initial aqueous solutions (blue and green squares) according to the CGWR_65 run in EQ3/6. Previous lake chemical compositions have been divided in three groups: water lake prior to the 2000 eruption (Cop 97–99) [*Varekamp et al.*, 2009], water lake just after the 2000 eruption (Cop 2001) [*Varekamp et al.*, 2009], water lake prior to the 2013 eruption (Cop 02–04) [*Varekamp et al.*, 2009], and water lake sampled in this work (Cop 2014).

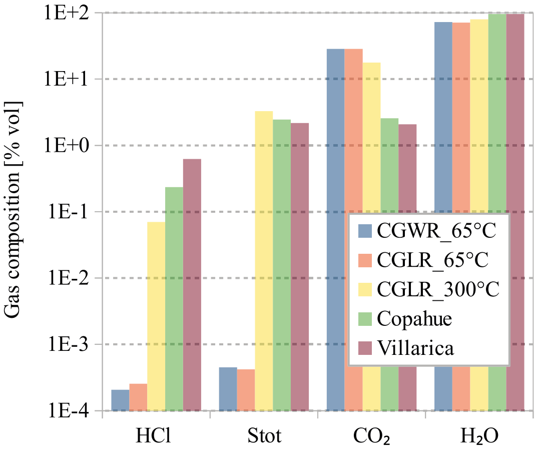

Figure 6. Calculated chemical composition of the gas phase released by single-step degassing of the end-of-run aqueous solution compared to the Copahue gas (this work) and Villarica gas [*Shinohara and Witter*, 2005].

with compositions of our Multi-GAS derived Copahue gas and the Villarica gas of *Shinohara and Witter* [2005] (our initial gas). The model-separated gases, formed after magmatic gas scrubbing at 65°C (CWLR_65°C and CGLR_65°C runs; see Table S2 in the supporting information), are largely depleted in acidic species (S_{TOT} and HCl <0.001 mol %) and H_2O (~28 mol %), compared to the initial (Villarica) gas, and appear dominated by less reactive CO_2 (~72 mol %). H_2S prevails over SO_2 among S species (H_2S/SO_2 molar ratio of 31–34) in these model-derived gases. These simulation results well represent, therefore, the extensive alteration of a pristine, formerly magmatic gas composition, upon interaction with a low-temperature aquifer system. We additionally note that these low-temperature model-separated gases are compositionally very dissimilar from our Multi-GAS based Copahue gas (Figure 6). The model-separated gas resulting from our 300°C runs (CWLR_300°C; see Table 2 in the supporting information) is comparatively more rich in sulfur (3.2–5.1 mol %) and chlorine (~0.06–0.07 mol %) relative to the 65°C runs (Figure 6), indicating that magmatic gas scrubbing has become less effective with increasing temperatures. This high-temperature model gas represents the ultimate product of equilibration of the magmatic gas phase in the sublimnic hydrothermal system underneath the lake and as such corresponds very well with the hydrothermal reservoir feeding the gas discharges, characterized by temperatures ranging from 250° to 300°C [*Agusto et al.*, 2013]. The 300°C model gases are also proportionally more H_2O rich (79 mol %) and CO_2 poor (16–18 mol %) but not to the extents seen in the natural gas samples (respectively ~95 mol % and 2–2.5 mol % for both Copahue and Villarica, see Figure 6).

5. Discussion

5.1. Magmatic Gas Fluxes

The SO_2 flux and plume chemical compositions, measured in 2014, are the first ever reported for Copahue. Our results overall demonstrate that Copahue was in 2014 one of the largest point sources of volcanic gas in arc context. The sizeable SO_2 flux emissions (~956 t d^{-1} as time average) detected by the UV camera were a factor ~3 higher than those inferred in November 1999 (~344 t d^{-1}) by *Varekamp et al.* [2001], based on measured river (Rio Agrio) flux data and modeled volcanic fluxes into the crater lake. Measurements of the SO_2 flux sustained by hyperacidic volcanic lakes worldwide are limited in number. Kawa Ijen (in Indonesia) and Poàs (in Costa Rica) volcanoes emit ~150 t d^{-1} [*Williams-Jones et al.*, 2010] and ~124 t d^{-1} [*Aiuppa et al.*, 2014], respectively. Modeled SO_2 emissions for a set of 14 volcanic lakes (for more details, see *Pasternack and Varekamp* [1997]) result in a maximum emission of ~600 t d^{-1} for Ruapehu (New Zealand). Copahue ranks therefore as of one of the strongest ever measured crater lake source of volcanic SO_2.

Our 2014 plume compositional data provide the basis for assessing the emission rates of H_2O, CO_2, H_2, HCl, and HBr from Copahue volcano. By scaling our averaged gas/SO_2 molar ratios to a SO_2 flux of 928 ± 386 t d^{-1}, we calculate fluxes for individual major gases (Table 2) and estimate a cumulative (total) gas output from the volcano of ~12,650 ± 5,110 t d^{-1}. Inferring the potential sources of these emissions is the objective of the following sections.

Table 2. Summary Table of Derived Volatiles Output

	SO_2	CO_2	H_2	H_2O	HCl	HBr	Total
Flux (t d^{-1})	956.00	637.53	3.29	10988.92	65.34	0.05	12651
Error	386	462	2.85	8390	43	0.06	7754

5.2. H_2O Flux Source

Copahue volcano was daily releasing ~11,000 tons of H_2O during our observations (Table 2). We argue this measured H_2O output was sustained by lake evaporation. To calculate the theoretical evaporation rate from Copahue Lake, we used the equation of *Weisman and Brutsaert* [1973]. This equation generally results in lower evaporative fluxes than other equations (see *Hurst et al.* [2012] for thorough discussion), but it has the advantage of fully accounting for the elevated ambient air temperature and humidity at the air-lake interface. In addition, earlier studies applied the same equation to similar crater lakes (i.e., Poas [*Brown et al.*, 1989]; Ruapehu [*Hurst et al.*, 1991]), which enables intercomparison of our results with earlier studies. The evaporative heat loss from the lake surface (in $\mathrm{W\,m^{-2}}$) was calculated from

$$LE(\mathrm{qw}-\mathrm{qa})u \tag{2}$$

where L is H_2O latent heat of vaporization (in $\mathrm{MJ\,kg^{-1}}$), E is the average particle flux; qw is the H_2O saturation concentration in air at lake temperature (in $\mathrm{kg\,m^{-3}}$), qa is H_2O concentration in air at ambient temperature (in $\mathrm{kg\,m^{-3}}$), and u is the friction velocity, a function of wind speed (in $\mathrm{m\,s^{-1}}$). For the measured lake water temperature (63°C), L is 2,354,000 $\mathrm{MJ\,kg^{-1}}$, E is 0.07431, and qw is 0.156 $\mathrm{kg/m^3}$ (at 100% humidity); for a wind speed of 2–6 $\mathrm{m\,s^{-1}}$ (considered as a representative range of the area), u is 0.076–0.228 $\mathrm{m\,s^{-1}}$; for a measured air humidity above the lake ranging from 18 to 70% and an ambient air temperature of 5–10°C, qa ranges from 0.149 to 0.154 $\mathrm{kg/m^3}$. Solving equation (2) for a maximum estimated lake surface area of ~26,000 $\mathrm{m^2}$ and an enthalpy of water at 63°C of ~2834 $\mathrm{kJ\,kg^{-1}}$, the evaporative flux from the surface of the crater lake ranges from ~1650 $\mathrm{t\,d^{-1}}$ to ~5000 $\mathrm{t\,d^{-1}}$ or ~16–50% of the measured surface H_2O flux. We can speculate that the "H_2O excess" (6000–9400 $\mathrm{t\,d^{-1}}$) represents the H_2O fraction correlated with the volcanic gases within the plume (e.g., with SO_2 in Figure 3b). Magmatic/hydrothermal steam emitted by fumaroles on the lake bottom should, in principle, condense instantaneously upon reaching contact with a ~60°C liquid (as also indicated by no evidence of bubble bursting at the lake surface); hence, if the H_2O excess were derived from a volcanic source, it should be sourced by vents outside the lake itself. However, no visible fumarole was observed during the March 2014 campaign. We propose, instead, that the H_2O excess may have been stripped away from the lake by the feeding volcanic gas stream (see below), in analogy to the process known in chemical engineering as "stripping" [*Bravo*, 1994]. Stripping is the physical separation process through which one or more components are removed from a liquid by a gas stream. During the process, the stripping gas (usually an inert gas) lowers the H_2O partial pressure, causing more H_2O to vaporize from the solution [*Campbell*, 2002; *Smith et al.*, 2004]. We suggest that this process may play an important role in degassing of volcanic lakes, which are characterized by a constant and high input of volcanic gases at the bottom.

5.3. Sources of Other Volatiles

While the lake itself might have been the source of the measured H_2O, via either evaporation or stripping, it is very unlikely that the same origin could have contributed the measured/calculated CO_2, SO_2, and HCl fluxes. The 2014 Copahue Lake, given its hyperacidic nature, contained small dissolved carbon, which partitioning into an evaporated lake gas phase would hardly have contributed our large, derived CO_2 flux (~638 $\mathrm{t\,d^{-1}}$; Table 2). We stress this plume CO_2 flux was substantial, e.g., ~4 times larger than that diffusely contributed by soils in the surrounding hydrothermal areas of Termas de Copahue, Las Machina, and Las Machinitas on March 2014 (~170 $\mathrm{t\,d^{-1}}$) (G. Chiodini et al., Carbon dioxide diffuse emission and thermal energy release from hydrothermal systems at Copahue volcano (Argentina), submitted to Journal of *Volcanology and Geothermal Research*, 2015). By normalizing our measured plume CO_2 flux by the satellite-estimated surface area of the lake (20,000–26,000 $\mathrm{m^2}$; calculated from the Google copyright satellite image taken on 1 May 2014, Figure 1b), we obtain a specific CO_2 flux of 25,600–33,250 $\mathrm{t\,d^{-1}\,km^{-2}}$. This number, when put in the context of CO_2 degassing regimes observed at other volcanic lakes in our Planet (range of surface-normalized CO_2 fluxes from 0.02 to 1485 $\mathrm{t\,d^{-1}\,km^{-2}}$) [*Pérez et al.*, 2011], makes of Copahue one of the greatest CO_2 degassing volcanic lakes.

We also suggest that lake evaporation could not account for the sizeable emissions of SO_2 (~956 $\mathrm{t\,d^{-1}}$) and HCl (~51 $\mathrm{t\,d^{-1}}$). Using the composition of the lake (Table 1c) and a lake mass ranging from $2.8\cdot10^4$ to $3.6\cdot10^4$, we infer the lake contained in March 2014 320–412 and 377–485 tons of SO_2 and HCl, respectively, which complete degassing would have been sufficient to supply plume gas emissions for 7–10 days at most. Given the persistent nature of plume degassing at Copahue, we conclude that an additional source of SO_2 and HCl must have been involved. Our measured HCl gas flux is very similar to the daily average HCl river flux estimated by *Varekamp et al.* [2001] over the last 20 years (~50 $\mathrm{t\,d^{-1}}$).

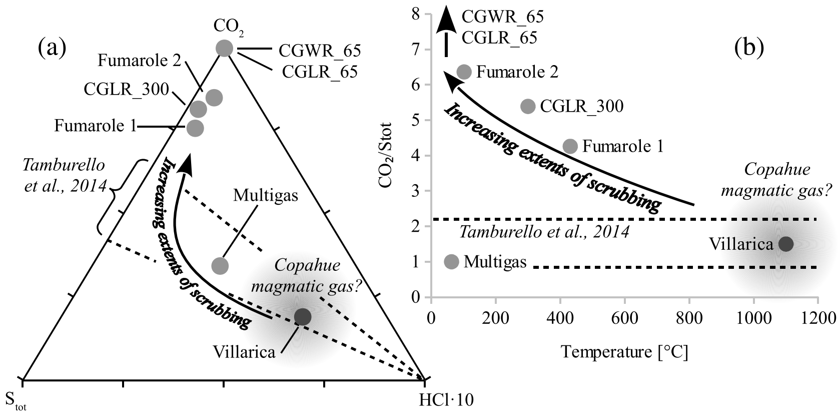

Figure 7. (a) Triangular CO_2-S_{tot}-HCl and (b) CO_2/S_{tot} VS temperature plots of the sampled gases and the gases of the end-of-run aqueous solutions. The dashed lines show the magmatic CO_2/S_{tot} fingerprint throughout the Chilean Arc suggested by *Tamburello et al.* [2014]. The shaded gray circle localizes a hypothetic compositional range for the Copahue magmatic gas.

Despite the presence of a crater lake, the Copahue gas plume exhibited in 2014 several of the typical compositional features of high-temperature magmatic gases, e.g., prevalence of SO_2 over H_2S, high halogen contents (Figure 7a), and low CO_2/SO_2 ratios (~1). The in-plume CO_2/SO_2 ratios were lower than those measured in the directly sampled 2013 fumarolic gases (Figure 7b) or in steam vents from the surrounding geothermal system [*Varekamp et al.*, 2001; *Agusto et al.*, 2013]; instead, they resulted more similar to the range of CO_2/SO_2 ratios characteristic of high-temperature gas emissions of other volcanoes of the andean volcanic front [*Shinohara and Witter*, 2005; *Tamburello et al.*, 2014] (Figure 7b). This, combined with the large 2014 fluxes that rank Copahue as an intermediate-to-high arc gas emitter [*Burton et al.*, 2013; *Shinohara*, 2013; *Oppenheimer et al.*, 2013], strongly supports a magmatic source of CO_2, SO_2, and HCl. We argue, therefore, that the measured Copahue gas emissions were largely sustained by the same numerous fumaroles that, visible on the crater bottom in 2013, had completely been covered by the acidic lake in 2014 (Figure 1d). This hypothesis, if correct, requires that gases emitted at the lake bottom could escape complete scrubbing by gas-rock-lake water reactions, to finally breach to the surface. The possible processes involved are discussed below.

5.4. Magmatic Gas-Lake Water Reactions

The similarity between Copahue gas and high-temperature magmatic gases from the Chilean arc [*Tamburello et al.*, 2014] (Figure 7b) overall suggests that gas-lake water interactions, and the consequent scrubbing of reactive soluble species (SO_2 and HCl), was minimized at Copahue in 2014. Our simulations of gas-water-rock interaction (Figures 5 and 6) indicate, in fact, that reaction of a magmatic (Villarica-type) gas at 65°C, if going to completion (e.g., reaching equilibrium), would yield to nearly complete scrubbing of magmatic S and Cl into the meteoric (CWLR_65°C) or lakwater (CGLR_65°C) aqueous solution. Ultimately, this process would lead to the formation of a residual, CO_2-dominated gas, after condensation into the aquifer/lake of magmatic steam. These 65°C model gas compositions are remarkably distinct from our Multi-GAS derived Copahue gas. We conclude, therefore, that the Copahue plume was not formed by equilibrium gas separation from the lake surface at 65°C and that a hotter environment of gas-water interaction was required instead. The temperature dependences of the equilibria [*Delmelle et al.*, 2000; *Kusakabe et al.*, 2000]

$$\mathrm{HCl} = \mathrm{H}^{+} + \mathrm{Cl}^{-}$$

$$3\mathrm{SO}_{2(aq)} + 2\mathrm{H}_2\mathrm{O}_{(l)} = \mathrm{S}_{o(s,l)} + 2\mathrm{HSO_4}^{-}{}_{(aq)} + 2\mathrm{H}^{+}{}_{(aq)}$$

dictate that increasing temperatures (at ultra-acidic pH conditions) shift both reactions toward the left [*Rouwet and Ohba*, 2015], favoring gas phase transport of HCl_g and SO_{2g}. As an effect of these reactions, our 300°C model run (CGLR_300°C) outputs a separated model gas that is richer in HCl and S than seen in low-T runs (CWLR_65°C and CGLR_65°C) (Figure 7b) and therefore more similar to the measured Copahue plume composition (Figure 7a). We propose this high-T run represents analogue for the natural case in which a high-T ($>>$ 300°C) gas phase, after partial re-equilibration in the hot (250–300°C) hydrothermal system underneath the lake, is rapidly injected into a hyperacid (pH ~0.5) lake. Under such conditions, the rapid transit of the gas inhibits equilibrium to be reached at shallow lake water conditions (65°C) but rather allows for a more S- and

Cl-rich (less scrubbed) gas to breach through the water surface (see Figure 6). Mixture of this poorly scrubbed, S-Cl-rich magmatic gas, with steam formed by lakewater evaporation, may finally have contributed the unusual composition of the "invisible" Copahue plume in 2014.

6. Conclusions

Our UV camera/Multi-GAS-based plume observations suggest a magmatic origin for the ongoing Copahue degassing unrest. We reveal that in March 2014, a naked eye invisible plume actively contributed a S-Cl-rich volcanic steam, at levels (~12,650 ± 5110 $t\,d^{-1}$) unusual for a volcanic lake but rather more comparable to those typical of an active open-vent arc volcano. The compositional signature (low CO_2/SO_2 ratios, high SO_2/H_2S ratios, and high halogen contents) of the 2014 Copahue gas was also fully consistent with leakage of hot magmatic fluids through the volcanic lake. Copahue is not an isolated case here, because high SO_2/H_2S, magmatic gas emissions have recently been reported for other volcanic lakes [*Shinohara et al.*, 2015]. These novel results suggest, therefore, that the volcanic gas supply underneath volcanic lakes is recurrently more oxidized and hotter ($SO_2/H_2S > 1000$) than the H_2S-rich fumaroles often encountered on the lakes' shore [this work; *Shinohara et al.*, 2015]. Based on observation and results of model simulations of magmatic gas-lake water reactions, we additionally conclude that scrubbing of water-soluble S and Cl can be substantially be reduced when a high flux magmatic gas stream is injected into (and rapidly travels throughout) a hyperacid volcanic lake. In such extreme conditions, evaporative losses from the lake can be intensified by H_2O stripping from the magmatic gas stream.

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