

# HCl degassing from extremely acidic crater lakes: preliminary results from experimental determinations and implications for geochemical monitoring

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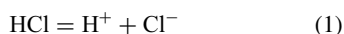
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**Abstract:** Crater lakes are monitored to detect volcanic unrest starting from the assumption that they behave as condensers for magmatic gases. A further assumption is that acidic gases such as HCl are conservative once dissolved in water. This is not true for extremely acidic crater lakes, whose H<sup>+</sup> activity is high enough to induce Cl<sup>-</sup> hydrolysis and consequently HCl degassing. This study presents the results of experimental determinations at 40–45°C demonstrating that HCl degassing from acidic water depends on pH and Cl<sup>-</sup> concentration. HCl degassing starts at pH values c. 0.05–0.1 with a rate of 5–10 mg min<sup>-1</sup> l<sup>-1</sup>, increasing up to c. 70 mg min<sup>-1</sup> l<sup>-1</sup> at pH < -0.2. This implies that the rate of HCl removal from a crater lake with a volume of 10<sup>4</sup>–10<sup>5</sup> m<sup>3</sup> and a seawater-like Cl<sup>-</sup> concentration ranges from 5 to 50 t h<sup>-1</sup>. The estimated HCl/H<sub>2</sub>O ratio in the separated vapour phase (0.01–0.2) is coherent with HCl/H<sub>2</sub>O ratios of fumaroles. Our experiments imply that: (i) the presence of very acidic gas species in fumaroles can be associated with a liquid-dominated feeding system, and (ii) dissolved in extremely acidic crater lakes, Cl<sup>-</sup> behaves as a non-conservative component.

Chlorine is volatile in the form of HCl, a strong acid that completely ionizes in aqueous solution according to the equation:



On one hand, this equation implies that when HCl released by a degassing magma at depth rises through water it will be completely dissolved and preserved as Cl<sup>-</sup> in the water phase. Moreover, chlorides do not significantly take part in mineral precipitation in hydrothermal environments. For these reasons Cl<sup>-</sup> is commonly considered a conservative element, useful as a geochemical tracer (Ingebritsen *et al.* 2001; Taran & Peiffer 2009). On the other hand, under extremely acidic conditions its conservative behaviour is not completely fulfilled: in the presence of a stronger acid than HCl, such as H<sub>2</sub>SO<sub>4</sub>, the H<sup>+</sup> excess obliges HCl to degas freely (Rouwet & Ohba 2015; Rouwet *et al.* 2016). The equilibrium in equation (1) shifts to the left, Cl<sup>-</sup> behaving as a conjugate base, leading to HCl degassing from the water body, and a coincident pH increase. Where SO<sub>2</sub> is merely scrubbed and retained more easily in the water phase as various

S species (bisulphate, thiosulphates, polythionates, elemental sulphur, etc.) (Symonds *et al.* 2001), HCl thus degasses due to the excess acidity. Simonson & Palmer (1993), on the basis of experimental data, provided the equation to estimate the partition coefficient *K* for HCl between liquid and vapour phase. According to these authors, HCl-partitioning in the vapour phase increases with increasing temperature and decreasing water density.

Active crater lakes typically dissolve magmatic gases, and are thus among the most acidic natural waters on Earth (Varekamp *et al.* 2000; Marini *et al.* 2003). Extremely acidic crater lakes are hosted by volcanoes such as Poás (Costa Rica; Rowe *et al.* 1992; Rouwet *et al.* 2016), Kawah Ijen (Java, Indonesia; Delmelle & Bernard 1994) and Copahue (Argentina–Chile; Varekamp *et al.* 2001; Tamburullo *et al.* 2015). The loss of HCl at the surface of a crater lake has been recognized since the 1980s at Poás (Rowe *et al.* 1992; Rouwet *et al.* 2014, 2016), manifested as increasing SO<sub>4</sub>/Cl ratios in lake water with time and decreasing lake volume. Recently, combined MultiGAS and alkaline trap measurements above Yudamari crater lake (Aso, Japan) have confirmed HCl degassing from an

acidic crater lake, with H<sub>2</sub>O/HCl proportions similar to adjacent fumaroles (Shinohara *et al.* 2015). Nevertheless, H<sub>2</sub>O MultiGAS measurements in extremely humid environments still incur high uncertainties (Gunawan *et al.* 2016). Moreover, in 2013–14 the Copahue crater lake released gases with a close-to-magmatic signature, showing that scrubbing of acidic gases was minimal, if it was occurring at all (Tamburello *et al.* 2015). In the latter study, HCl degassing (flux) was quantified for the first time. Nevertheless, the transition from hydrolysed Cl<sup>-</sup> to gaseous HCl at the lake surface, deduced from the water chemistry rather than the plume chemistry, is still poorly constrained.

Active crater lakes are the open-air proxy of a magmatic–hydrothermal system feeding high-temperature fumaroles. A subsurface analogue of a high-temperature acidic brine where HCl partitions in a vapour phase was identified after HCl-induced corrosion of well casings in (superheated) geothermal systems (Truesdell *et al.* 1989). Even more acidic surface waters, although partly ‘man-made’, are found in mine pit lakes (pH values as low as -3.4; Nordstrom *et al.* 2000). These lakes, however, lack Cl<sup>-</sup> as they formed after leaching of high-sulphidation ore deposits, and the acidity is generated by oxidation of pyrite from metal sulphide deposits. The lack of Cl<sup>-</sup>, and thus HCl release, is arguably the main reason why mine pit lakes can be even more acidic than active crater lakes.

Quantitative insights into the degassing dynamics of HCl through an active crater lake permit the quantification of the HCl input from magmatic degassing beneath the crater lake. This has implications for the surveillance of volcanoes that host crater lakes (e.g. Poás, Rincón de la Vieja, Copahue, Ruapehu, White Island, Kawah Ijen, Aso and Kusatsu-Shirane), as tracking the crater lake water chemistry over time has not always been the most straightforward means to forecast changes in unrest on the short term (e.g. phreatic eruptions), due to the temporal (residence-time-dependent monitoring window; Rouwet *et al.* 2014, 2016) and spatial (localized eruptive vents) limitations of lake hydrodynamics. A major aim of this study is to deepen our insights in the kinetics of HCl degassing from an acidic crater lake, as recent work has demonstrated that this is far from an equilibrium process.

## Experimental setup

In this study, we mimic acidic crater lakes in the laboratory using an SO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup>-rich solution with 1 M NaCl, acidified with H<sub>2</sub>SO<sub>4</sub> 0.5 M (i.e. an initial pH of 0.3), and set at a temperature of 40–45°C. To better simulate the open-system behaviour of a summit crater lake, often subjected to windy conditions, the

solution is stored in a pyrex beaker with a volume of 1.5 l and positioned within an aspiration hood set at *c.* 150 m<sup>3</sup> h<sup>-1</sup>, which corresponds to a wind speed of *c.* 5 m s<sup>-1</sup>. The residual solution is weighted and sampled every hour with a 10 ml plastic syringe (*c.* 1 ml of sample). This aliquot is diluted 100 times immediately after sampling, then measured and titrated (see below) for pH and analysed for its Cl<sup>-</sup> content. The removal of about 1 ml for each sample from the solution involves an overall change of volume of about 4%, totally irrelevant for the purposes of the experimental results. This procedure results in empirical relationships between the Cl<sup>-</sup> content and time (i.e. flux), temperature, pH and residual ‘lake’ volume.

Measuring the pH in extremely acidic environments may be subject to significant errors and uncertainties due to: (i) non-linear solution behaviour; (ii) non-linear and irreversible electrode response; and (iii) inappropriate use of the conventional definition of pH. In the experimental setup, the theoretical pH at different steam separation steps was calculated according to two different approaches. The first is pH as  $-\log m_{\text{H}^+}$ , which considers complete dissociations of the diprotic H<sub>2</sub>SO<sub>4</sub>. The second provides estimates of the single-ion activity coefficient for protons based on the Pitzer approach ( $-\log a_{\text{H}^+}$ ; Nordstrom *et al.* 2000). Measurements of pH were carried out for each sample step on the diluted aliquot to estimate the free protons by using a combined glass electrode with a 3 M KCl filling solution. This measured value can be considered to be closest to the conventional definition of pH (i.e. the Pitzer approach). The ‘total’ protons available (i.e. the total stored acidity (TSA) on complete dissociation of H<sub>2</sub>SO<sub>4</sub>; calc. II diss. in Table 1) were detected by an alkaline titration with a 0.1 M NaOH solution. Ion chromatography equipment was used to measure the Cl<sup>-</sup> contents using standard techniques.

## Results: HCl degassing and pH measurements

The results of two days of 20 experimental steps are reported in Tables 1 and 2. The weight of the residual solution as well as the amount of vapour loss are reported in Table 1. The experiment started with 511 g of solution at pH = 0.3. The amount of vapour loss for each step ranges between 8.74 and 65.80 g. Owing to the removal of solution, the nominal H<sub>2</sub>SO<sub>4</sub> concentration increases from an initial 0.501 M to a final 2.571 M, assuming that no S volatile species is lost by degassing. For the purpose of the experiment (i.e. to quantify HCl degassing), this assumption is reasonable as SO<sub>2</sub> degassing does not affect the pH of the residual solution. As

**Table 1.** Theoretical and measured acidity of the 20 experimental steps

Steps	Weighted solution (g)	Vapour loss (g)	H <sub>2</sub> SO <sub>4</sub> (mol kg <sup>-1</sup> )	pH <sub>(Pitzer model)</sub> after vapour loss	pH <sub>(calc. II diss.)</sub> after vapour loss	H <sup>+</sup> titrated (mol l <sup>-1</sup> )	pH <sub>tot</sub> titrated	H <sup>+</sup> measured (mol l <sup>-1</sup> )	pH measured
0.3-1	445.20	65.80	0.575	0.23	-0.06	1.04	-0.02	0.39	0.40
0.3-2	434.51	10.69	0.589	0.22	-0.07	1.02	-0.01	0.30	0.53
0.3-3	384.70	49.81	0.665	0.16	-0.12	1.25	-0.10	0.61	0.22
0.3-4	369.48	15.22	0.693	0.14	-0.14	1.26	-0.10	0.62	0.21
0.3-5	359.01	10.47	0.713	0.13	-0.15	1.71	-0.23	0.88	0.05
0.3-6	344.02	14.99	0.744	0.11	-0.17	1.35	-0.13	0.66	0.18
0.3-7	330.05	13.97	0.776	0.09	-0.19	1.41	-0.15	0.69	0.16
0.3-8	317.03	13.02	0.808	0.07	-0.21	1.46	-0.16	0.76	0.12
0.3-9	304.03	13.00	0.842	0.05	-0.23	1.50	-0.18	0.74	0.13
0.3-10	292.78	11.25	0.874	0.04	-0.24	1.55	-0.19	0.76	0.12
0.3-11	248.48	44.30	1.030	-0.06	-0.31	1.85	-0.27	0.91	0.04
0.3-12	229.16	19.32	1.117	-0.10	-0.35	1.95	-0.29	0.92	0.03
0.3-13	202.74	26.42	1.263	-0.16	-0.40	2.12	-0.33	1.03	-0.01
0.3-14	187.59	15.15	1.365	-0.22	-0.44	2.28	-0.36	1.10	-0.04
0.3-15	178.85	8.74	1.431	-0.25	-0.46	2.85	-0.45	1.16	-0.06
0.3-16	166.10	12.75	1.541	-0.30	-0.49	2.48	-0.39	1.25	-0.10
0.3-17	137.59	28.51	1.861	-0.49	-0.57	1.53	-0.18	1.40	-0.15
0.3-18	128.39	9.20	1.994	-0.55	-0.60	3.06	-0.49	1.52	-0.18
0.3-19	118.97	9.42	2.152	-0.59	-0.63	6.62	-0.82	3.18	-0.50
0.3-20	99.58	19.39	2.571	-0.59	-0.71	11.66	-1.07	4.89	-0.69

For details see text.

**Table 2.** Theoretical and measured  $\text{Cl}^-$  concentrations in the residual solutions during the 20 experimental steps

Steps	Weighted solution (g)	Vapour loss (g)	Fraction of residual vapour	$\text{Cl}^-_{\text{meas}}$ ( $\text{mg l}^{-1}$ )	$\text{Cl}^-_{\text{calc}}$ ( $\text{mg l}^{-1}$ )	$\text{Cl}^-_{\text{calc}}^*$ ( $\text{mg l}^{-1}$ )	Time elapsed (min)	$\text{Cl}^-$ loss (mg)	$\text{Cl}^-$ loss* (mg)	$\text{Cl}^-$ exsolution rate ( $\text{mg min}^{-1}$ )	$\text{Cl}^-^*$ exsolution rate ( $\text{mg min}^{-1}$ )	HCl loss (mg)	HCl/vapour (wt/wt)
0.3-1	445.20	65.80	0.87	37 792									
0.3-2	434.51	10.69	0.85	38 750	38 722	38 722	45	0.0	0.0	0.00	0.00	0.00	0.00
0.3-3	384.70	49.81	0.75	43 753	43 735	43 767	n.d.	0.0	0.0	0.00	0.00	0.00	0.00
0.3-4	369.48	15.22	0.72	45 778	45 537	45 555	n.d.	0.0	0.0	0.00	0.00	0.00	0.00
0.3-5	359.01	10.47	0.70	46 554	46 865	47 113	48	111.6	200.7	2.33	4.18	206.37	0.02
0.3-6	344.02	14.99	0.67	47 912	48 907	48 582	n.d.	342.3	230.7	n.d.	n.d.	237.17	0.02
0.3-7	330.05	13.97	0.65	50 546	50 977	49 940	60	142.3	0.0	2.37	0.00	0.00	0.00
0.3-8	317.03	13.02	0.62	52 356	53 071	52 622	60	226.6	84.3	3.78	1.40	86.66	0.01
0.3-9	304.03	13.00	0.59	54 162	55 340	54 595	n.d.	358.1	131.5	n.d.	n.d.	135.26	0.01
0.3-10	292.78	11.25	0.57	55 416	57 466	56 243	50	600.3	242.2	12.01	4.84	249.01	0.02
0.3-11	248.48	44.30	0.49	65 501	67 712	65 296	n.d.	549.3	0.0	0.00	0.00	0.00	0.00
0.3-12	229.16	19.32	0.45	69 613	73 420	71 023	85	872.5	323.2	10.26	3.80	332.29	0.02
0.3-13	202.74	26.42	0.40	75 559	82 988	78 685	110	1506.2	633.7	13.69	5.76	651.56	0.02
0.3-14	187.59	15.15	0.37	81 581	89 690	81 661	80	1521.2	15.1	19.02	0.19	15.48	0.00
0.3-15	178.85	8.74	0.35	85 170	94 073	85 568	45	1592.3	71.1	35.39	1.58	73.13	0.01
0.3-16	166.10	12.75	0.33	88 486	101 294	91 708	65	2127.5	535.1	32.73	8.23	550.23	0.04
0.3-17	137.59	28.51	0.27	103 508	122 284	106 821	n.d.	2583.3	455.9	n.d.	n.d.	468.72	0.02
0.3-18	128.39	9.20	0.25	106 148	131 046	110 925	60	3196.7	613.3	53.28	10.22	630.63	0.07
0.3-19	118.97	9.42	0.23	107 779	141 422	114 553	65	4002.5	805.9	61.58	12.40	828.61	0.09
0.3-20	99.58	19.39	0.19	90 197	168 960	128 765	n.d.	7843.2	3840.7	n.d.	n.d.	3948.99	0.20
Total loss		345.62						7843.2				8064.43	0.02

$\text{Cl}^-_{\text{calc}}^*$  is the calculated increase in concentration by using the measured  $\text{Cl}^-$  in the previous step; n.d., not detected.

## HCl DEGASSING FROM ACIDIC CRATER LAKES

expected, given the pH range of the experiment and the  $pK_1$  and  $pK_2$  of  $H_2SO_4$  ( $-2$  and  $1.9$ , respectively), the most dominant species of sulphuric acid is  $HSO_4^-$ , hence the pH values calculated according to the single-ion activity coefficient estimates for protons based on the Pitzer approach do not significantly deviate from those of a complete first dissociation. This is particularly evident for the first 7–8 steps, but the deviation increases in the following steps. Finally, Table 1 reports the measured pH in two different ways: by  $OH^-$  ( $0.1$  M) titration, and by direct pH measurements with a glass electrode in the diluted aliquots. As reported in the previous section, the first method provides the total titrated acidity (TTA), whereas the second estimates the concentration of the free protons. As expected, the TTA increases with decreasing residual solution, but, as shown in Figure 1, it has a non-linear correlation with the calculated pH after complete  $H_2SO_4$  dissociation (TSA). Up to  $pH -0.55 \pm 0.05$ , the TTA is lower than the TSA (Fig. 1), possibly due to  $Cl^-$  hydrolysis and HCl degassing. With less residual solution the TTA unexpectedly becomes higher than the TSA, providing a theoretical  $pH < -1.0$ . This effect can only be explained by precipitation of sodium sulphate in its less soluble, hydrated form ( $Na_2SO_4 \cdot 10H_2O$ , mirabilite), as observed in the two last steps. Table 2 provides the calculated (both cumulated and step-by-step values) and measured  $Cl^-$  concentrations during vapour separation steps. The calculated  $Cl^-$  concentration is obtained by recalculating for the amount of steam loss, assuming that HCl is not lost from solution. In Figure 2 the measured  $Cl^-$  concentrations are plotted against the calculated ones (the cumulated values). According to

the observed distribution, the measured values become significantly lower with respect to the calculated ones when pH decreases to  $<0.05-0.1$  and this deviation drastically increases at  $pH < -0.20$ . During the last step of vapour loss, which is characterized by a *c.* 0.2 liquid residual fraction and a pH value of *c.*  $-1.0$ , the relative loss of  $Cl^-$  is higher (30%) with respect to that of the water solution (19%). The resulting HCl/ $H_2O$  weight ratios in the separated steam range between 0.01 and 0.20 (average 0.02), the latter value corresponding to the last separation step. Such HCl/ $H_2O$  ratios are three orders of magnitude higher than for equilibrium degassing from a pure HCl solution (Washburn 1928; Shinohara *et al.* 2015), suggesting that HCl degassing under conditions of  $H^+$ -excess (from  $H_2SO_4$ ) is a kinetics-dominated process. As shown in Figure 3 ( $Cl^-$  loss v. the fraction of the residual solution for each separation step), the rate of HCl removal at a pH value of *c.*  $0.05-0.1$  is  $5-10$   $mg\ min^{-1}\ l^{-1}$  and it increases to  $>70$   $mg\ min^{-1}\ l^{-1}$  at  $pH < -0.20$ .

## Discussion

### *The crater lake as a fumarole feeding system*

It is often observed that fumaroles at boiling temperature are free of the acidic gas species, as these are completely scrubbed in the feeding aquifer. Degassing of acid species from boiling temperature fumaroles has been temporarily detected at just a few volcanoes (Turrialba, Tacora and Meakandake), often preceding phreatic eruption activity and probably triggered by the input of a hot magmatic gas

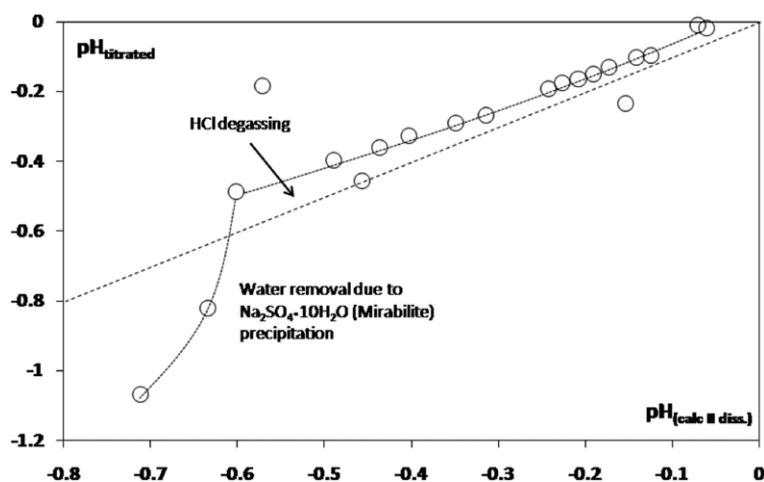
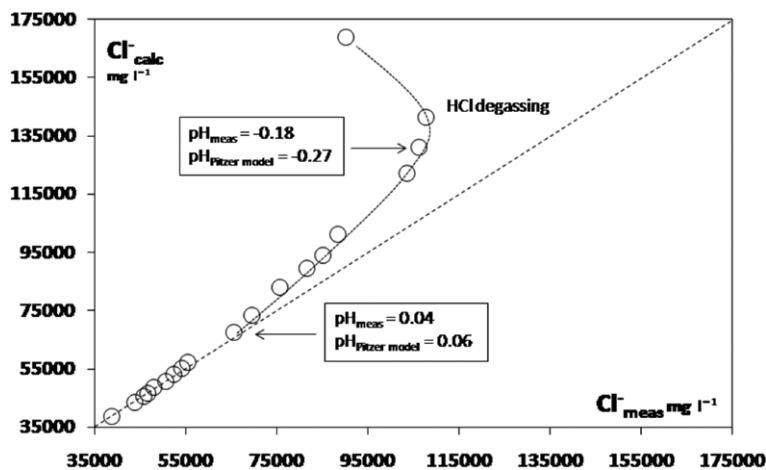


Fig. 1. pH values for the different steps based on  $OH^-$  ( $0.1$  M) titration v. the calculated pH values based on a complete  $H_2SO_4$  dissociation (the TSA). The dashed line represents equivalent values.

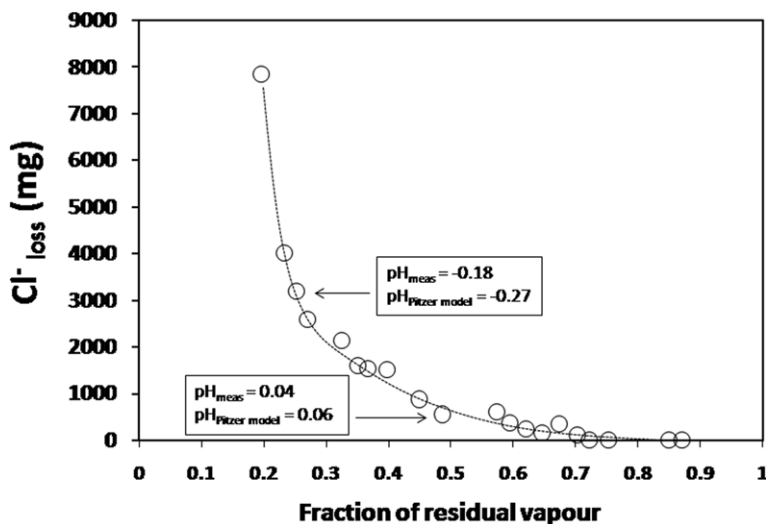


**Fig. 2.** Measured v. calculated  $\text{Cl}^-$  concentrations (cumulated) for the different experimental steps. The dashed line represents equivalent concentrations.

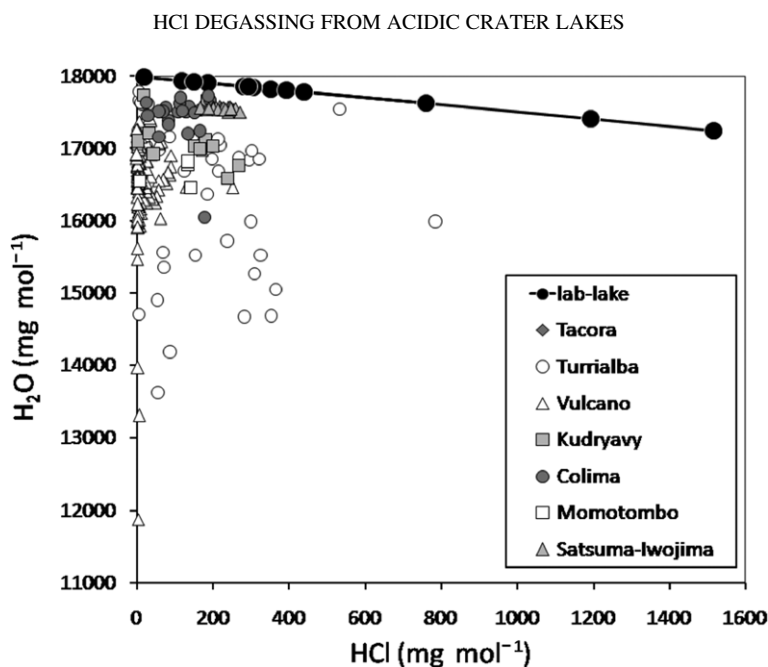
phase (Vaselli *et al.* 2009; Capaccioni *et al.* 2011; Shinohara *et al.* 2011).

The observed  $\text{HCl}/\text{H}_2\text{O}$  ratios of the lab-lake experiment seem to be largely coherent with the measured values in fumaroles of both high and low temperatures at actively degassing volcanoes. Figure 4 compiles  $\text{HCl}/\text{H}_2\text{O}$  ratios for Tacora (Chile), Turrialba (Costa Rica), Vulcano (Italy), Kudryavy (Kuril Islands), Colima (Mexico), Momotombo (Nicaragua) and Satsuma Iwojima (Japan), and compares them with the measured  $\text{HCl}/\text{H}_2\text{O}$  ratios for the gas–vapour mixture released at the

experimental lab-lake. Despite the low-temperature experimental conditions (40–45°C), the gas coming off the lab-lake contains more  $\text{HCl}$  than the fumaroles, regardless of their temperature (Fig. 4). The results of our experiment imply that: (i)  $\text{HCl}$  can degas from low-temperature (boiling or even lower temperature), if the reigning aquifer conditions are extremely acidic; and (ii) high-temperature fumaroles do not need ‘dry-gas’ conditions to release acidic gas species such as  $\text{HCl}$ . In other words, the occurrence of very acidic, water-soluble components in fumarolic gases is not necessarily



**Fig. 3.** The cumulate loss of  $\text{Cl}^-$  v. the fraction of residual solution. The trend suggests a rapid increase of degassing rate with increasing acidity and  $\text{Cl}^-$  concentration.



**Fig. 4.** HCl/H<sub>2</sub>O ratios for Tacora (Chile,  $T = 82\text{--}93^\circ\text{C}$ ; Capaccioni *et al.* 2011), Turrialba (Costa Rica,  $T = 88\text{--}282^\circ\text{C}$ ; Vaselli *et al.* 2009), Vulcano (Italy,  $T = 200\text{--}450^\circ\text{C}$ ; personal data), Kudryavy (Kuril Islands,  $T = 130\text{--}940^\circ\text{C}$ ; Taran *et al.* 1995), Colima (Mexico,  $T = 370\text{--}820^\circ\text{C}$ ; Taran *et al.* 2002), Momotombo (Nicaragua,  $T = 105\text{--}790^\circ\text{C}$ ; Menyailov *et al.* 1986), Satsuma-Iwojima (Japan,  $T = 848\text{--}886^\circ\text{C}$ ; Shinohara *et al.* 2002) and for the HCl-rich vapour coming off the lab-lake.  $T$ , temperature.

related to the absence of liquid water in the feeding conduits.

#### *HCl budget analyses and magmatic input flux*

The paradigm that  $\text{Cl}^-$  is a conservative element in the aqueous system is disproved by the lab-lake experiment: under extremely acidic conditions HCl is a volatile rather than a hydrophile. HCl degassing is manifested in nature at high-acidity crater lakes. A crater lake is an open system, therefore the estimated HCl removal rate at  $40\text{--}45^\circ\text{C}$ , negative pH and seawater-like  $\text{Cl}^-$  concentrations enables to estimate the total emission rate. For instance, a crater lake with a volume of  $10^4\text{--}10^5\text{ m}^3$  and a seawater-like  $\text{Cl}^-$  concentration containing about  $38 \times 10^4\text{--}10^5\text{ kg}$  of  $\text{Cl}^-$  will remove 5–50 tons of HCl per hour.

This means that in an open system an equivalent amount of the  $\text{Cl}^-$  contained in the lake is transferred as HCl to the atmosphere within a few days. Eventually, in the case of steady-state lake conditions (pH,  $\text{Cl}^-$  concentration, temperature and lake volume) this suggests an input flux of at least the same order of magnitude from the underlying magmatic degassing system. Figure 5a and b show the conditions of the crater lake of Copahue volcano in 2005 and 2012, respectively. Evidence of diffuse

degassing from the lake was first observed in 2011 and significantly increased up to the end of 2012. This progressive evolution ended with a vulcanian/strombolian eruption on 22 December 2012.

#### **Conclusions and implications for volcanic surveillance**

We mimicked extremely acidic crater lake conditions in a laboratory experiment. An  $\text{SO}_4^-$  and Cl-rich solution with 1 M NaCl, acidified with 0.5 M  $\text{H}_2\text{SO}_4$  to an initial pH of 0.3 was heated at  $40\text{--}45^\circ\text{C}$  and left to evaporate as an open system for two days. Samples from the remaining solution were collected more or less on an hourly basis. The lab-lake became concentrated in  $\text{H}^+$  and  $\text{Cl}^-$  over time, leading to increased acidity and HCl degassing, accompanied by water evaporation. The observed HCl/H<sub>2</sub>O weight ratios (0.01–0.2) were similar to those measured in fumarolic emissions, regardless of the temperature of the fumaroles. These observations imply that: (i) HCl is not conservative under extremely acidic conditions (the HCl degassing rate becomes significant at  $\text{pH} < 0.05$ ); and (ii) an acidic crater lake can be considered an open-air analogue of a parent fluid for fumarolic emissions.





**Fig. 5.** The crater lake of Copahue volcano: (a) December 2004; (b) July 2012.

The outcome of this experiment has strong implications for volcanic surveillance using crater lake composition, but also for fumarole geochemistry as a monitoring tool. The sensitivity of a crater lake and the effectiveness of tracking variations in crater lake water chemistry in monitoring setups were thought to largely depend on the lake water residence time (i.e. lake volume ( $\text{m}^3$ )/fluid input or output rate ( $\text{m}^3 \text{s}^{-1}$ ); Varekamp 2002; Rouwet *et al.* 2014). Smaller and fast-flushing lakes are thus more sensitive and their chemistry can reveal information on the short term. Classically,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations are the most indicative parameters related to magmatic degassing (Varekamp *et al.* 2000). However, the quantitative approach used in this study shows that the  $\text{Cl}^-$  content in

crater lake water instead reflects a transient condition of a gas pulse rising through the lake: only part of the  $\text{HCl}$  will be scrubbed in the lake water, while a considerable part will be released as a gas at the lake surface. From this new viewpoint, the sensitivity of an active crater lake as a monitoring tool is increased, but only if we understand the processes and kinetics of why and how  $\text{Cl}$  partitions between the gas and liquid phases as the gases rise through extremely acidic water. Moreover, we assumed here that the stronger acid  $\text{SO}_2$  stays in solution, whereas  $\text{SO}_2$  is known to be released from acidic crater lakes (Shinohara *et al.* 2015; Tamburullo *et al.* 2015; Gunawan *et al.* 2016). Besides the extremely complex sulphur-speciation in crater lake environments (Delmelle & Bernard 2015;



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Henley 2015), how SO<sub>2</sub> behaves with respect to HCl in the aqueous acidic environment is not yet clear. Thus far, temporal variations of SO<sub>4</sub>/Cl ratios could only be interpreted in a qualitative way (e.g. Rowe *et al.* 1992; Rouwet *et al.* 2016).

Variations in the chemistry of fumaroles have been assumed to reflect almost real-time indicators of the changes in the degassing regime of a volcano, and thus tracked to monitor activity. With the observation of acidic gas species in boiling-temperature fumaroles (Turrialba, Tacora, Meakan-dake; Vaselli *et al.* 2009; Capaccioni *et al.* 2011; Shinohara *et al.* 2011), and HCl degassing at even lower-temperature conditions (this study), the presence of an extremely acidic aquifer beneath fumaroles has also temporal buffer capacities. The hydrodynamics in aquifers is even slower than for lakes (low porosity/permeability v. open-water systems), and could thus additionally slow down the signal of a fumarole at the surface. The appearance of acidic gases in a fumarole (e.g. Turrialba; Vaselli *et al.* 2009) could suggest that the parent aquifer is becoming strongly acidified and/or that the rock buffer capacity is exhausted. Acidifying a previously non-acidic aquifer to a pH near 0 requires a large input of acidic gases, which requires time.

Both fumaroles and lake systems are prone to phreatic eruptive activity. This study indicates that for crater lake systems, a combination of water and gas chemistry (fluxes and gas ratios at the lake surface) provides a more adequate monitoring tool than water chemistry alone. For fumaroles, however, HCl scrubbing and eventual HCl degassing will have a delaying effect: the aquifer slows down the ascent of gas from a magma. This implies that the input of a magmatic fluid preceding (phreatic) eruptions can arrive before the chemical signal can be detected at the surface, which is probably one of the reasons why (phreatic) eruptions at hydrothermal systems remain highly unpredictable.

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