Chlorine isotope and Cl–Br fractionation in fluids of Poás volcano (Costa Rica): Insight into an active volcanic–hydrothermal system

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ABSTRACT

Halogen-rich volcanic fluids issued at the surface carry information on properties and processes operating in shallow hydrothermal systems. This paper reports a long-term record of Cl–Br concentrations and $\delta^{37}Cl$ signatures of lake water and fumaroles from the active crater of Poás volcano (Costa Rica), where surface expressions of magmatic-hydrothermal activity have shown substantial periodic changes over the last decades. Both the hyperacid water of its crater lake (Laguna Caliente) and subaerial fumaroles show significant temporal variability in Cl–Br concentrations, Br/Cl ratios and $\delta^{37}Cl$, reflecting variations in the mode and magnitude of volatile transfer. The $\delta^{37}Cl$ signatures of the lake, covering the period 1985–2012, show fluctuations between $+0.02 \pm 0.06‰$ and $+1.15 \pm 0.09‰$. Condensate samples from adjacent fumaroles on the southern shore, collected during the interval (2010–2012) with strong changes in gas temperature (107–763°C), display a much larger range from $-0.43 \pm 0.09‰$ to $+14.09 \pm 0.08‰$. Most of the variations in Cl isotope, Br/Cl and concentration signals can be attributed to interaction between magma-derived gas and liquid water in the volcanic–hydrothermal system below the crater. The $\delta^{37}Cl$ were lowest and closest to magmatic values in (1) fumarolic gas that experienced little or no interaction with subsurface water and followed a relatively dry pathway, and (2) water that captured the bulk of magmatic halogen output so that no phase separation could induce fractionation. In contrast, elevated $\delta^{37}Cl$ can be explained by partial scavenging and fractionation during subsurface gas–liquid interaction. Hence, strong Cl isotope fractionation leading to very high $\delta^{37}Cl$ in Poás' fumaroles indicates that they followed a wet pathway. Highest $\delta^{37}Cl$ values in the lake water were found mostly in periods when it received a significant input from subaqueous fumaroles or when high temperatures and low pH caused HCl evaporation. It is concluded that combined monitoring of $\delta^{37}Cl$ and Br/Cl in Laguna Caliente and adjacent fumaroles provides valuable information on activity in the subsurface hydrothermal system with significant relevance for volcanic surveillance of Poás.

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1. Introduction

Chlorine and bromine are generally extracted from degassing magma in the form of $HCl_{(g)}$ and $HBr_{(g)}$ (Gerlach, 2004; Aiuppa et al., 2005; Martin et al., 2006). While chlorine is generally the most abundant halogen in volcanic gases (Taran and Zelenski, 2015), bromine is present in amounts that are orders of magnitude lower. Gerlach (2004) reported an average molar Br/Cl ratio of 0.0022 ± 0.0020 for high-temperature gas condensates from arc volcanoes. Upon shallow emplacement of magma, both halogens are expelled during cooling and crystallizing, driven by their relatively high H_2O vapour/melt partition coefficients (Villemant and Boudon, 1999; Balcone-Boissard et al., 2010). In subsurface volcanic hydrothermal systems associated with intrusions, they tend to be concentrated in fluid phases, showing a strongly hydrophilic behaviour. Since shallow hydrothermal processes can fractionate Cl and Br (Berndt and Seyfried, 1990, 1997; Lüders et al., 2002; Liebscher et al., 2006; Foustoukos and Seyfried, 2007), the proportions of these halogens in volcanic fluids are potential signals of interaction and separation processes in the trajectory between magma and atmosphere, such as boiling, condensation, evaporation, mixing and mineral precipitation (Villemant et al., 2003, 2005, 2014; Wu et al., 2012; Fischer et al., 2015). Likewise, the chlorine isotope compositions of fluids from shallow magma degassing are sensitive to fractionation during interaction between deep gases and shallow water bodies within a volcanic edifice (Sharp et al., 2010; Li et al., 2015). Volcanic fumaroles confirm this since the available data show large $\delta^{37}Cl$ variations compared to other terrestrial materials (Eggenkamp, 1994; Wahrenberger et al., 1997; Musashi and Eggenkamp, 2000; Barnes et al., 2008; Sharp et al., 2010; Rizzo et al., 2013).

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This paper explores the extent and causes of Cl–Br and chlorine isotope fractionation using time series data for fluids from the active crater of Poás volcano (Costa Rica). Samples were taken from its hyper-acid lake (Laguna Caliente) and from a persistently active fumarole field on the southern shore. The lake data cover a period of almost three decades (1985–2012) when marked changes in activity and physico-chemical properties were recorded (Rowe et al., 1992a, 1992b; Martínez et al., 2000; Martínez, 2008; Rouwet et al., 2016; and references therein). The fumarole data represent a two-year interval (2010–2012) in which the temperatures ranged between 763 and 107 °C, and showed a declining trend. For a preceding period (2001–2007), Sharp et al. (2010) documented a strong δ^{37}Cl fractionation in other (low-temperature) fumaroles that were temporarily active within the crater, and attributed this to a distillation-recondensation process within the plumbing system. Fischer et al. (2015) presented data sets on the chemical and isotopic compositions of fumarolic discharges that cover both periods. Our results demonstrate that halogen signatures of Laguna Caliente and associated fumaroles signal active magma-gas–liquid interaction processes in the subsurface volcanic–hydrothermal system of Poás. The observed time series trends, in conjunction with other chemical parameters recorded at this volcano, provide insights into the potential of chlorine and bromine for monitoring purposes as an aid to mitigate hazards from eruptive activity.

2. Geological setting

Quaternary volcanism in Central America is associated with sub-duction of the Cocos plate under the Caribbean plate. The convergence offshore from Nicoya Peninsula in Costa Rica occurs at a rate of 74–85 mm/yr at 20–22° azimuth (DeMets et al., 2010). Poás, in the Cordillera Central of Costa Rica (Fig. 1), is a complex basaltic andesitic stratovolcano with a maximum elevation of 2708 m.a.s.l. Erupted products mainly consist of calc-alkaline basaltic and andesitic lavas and pyroclastics (Prosser and Carr, 1987; Cigolini et al., 1991; Malavassi, 1991). Its 1.3 km wide active crater hosts an acidic lake known as Laguna Caliente in a 300 m-diameter pit, and a ~30 m high pyroclastic cone, which is a site of persistent fumarolic activity (Fig. 2). The structure is often referred as "the dome" but since it is composed of tephra from the 1953–55 eruption (Casertano et al., 1987), we will use the term "composite pyroclastic cone" or "CPC", following Martínez et al. (2000) and Martínez (2008). This 1953–55 eruption was the latest with juvenile materials. Such events are relatively rare at Poás, in contrast to the frequent occurrences of phreatic explosions.

Over the last decades, the water of Laguna Caliente has shown pH values ranging between −0.87 and 1.75, and temperatures from 22 to 94 °C (Martínez, 2008). Concentrations of sulphate (3300–285,000 mg/kg or 34–297 mmol/kg) and chloride (2500–15,000 mg/kg or 70–3244 mmol/kg) fluctuate but have been always extremely high, which also holds for dissolved rock-forming elements (Rowe and Brantley, 1993; Martínez, 2008). The activity of the crater area is characterized by a long history of intermittent phreatic eruptions and persistent fumarolic emissions. Martínez (2008) subdivided the activity of Poás since the early 1970's into five stages. During Stage I (1972–August 1980), fumarolic discharges were strong within the lake and were accompanied with occasional phreatic explosions. Stage II (September 1980–April 1986) was characterized by a relative quiescence in the lake and absence of phreatic activity despite a strong discharge of high-temperature fumaroles through the CPC. In 1981,

Fig. 1. Location map of Poás volcano.

Fig. 2. Poás volcano (May 2012), view from the NE rim of the active crater towards Laguna Caliente and the composite pyroclastic cone (CPC).

preceded by a regional earthquake, an inferred rupture of the carapace of a magma body at depth, possibly accompanied by a localized intrusion of gas-rich magma beneath the CPC, triggered an increase in fumarole temperatures from 92 to 1020 °C (Casertano et al., 1987; Rymer et al., 2000), the highest temperatures ever recorded in the fumaroles of Poás volcano. In the following Stage III (May 1986 - August 1995), a vigorous subaqueous fumarolic discharge and intense phreatic activity accompanied a strong volume decrease, ultimately leading to a dry-out of the lake. The gradual drop of the lake level in 1987–89 revealed a muddy floor with numerous boiling mud pools where ~1–3 m high yellow ephemeral cones of sulphur and pyroclastic materials formed, acting as sites of vigorous gas emissions (Oppenheimer and Stevenson, 1989). Stage IV (September 1995–February 2005) was a calm period, when the lake re-established and subaerial fumaroles and hot springs appeared in the surrounding crater area (Vaselli et al., 2003). Stage IV was followed by an intense fumarolic discharge into the lake during Stage V (March 2005–present) together with frequent phreatic eruptions since March 2006 and a steady decrease of the lake volume. This episode may have been triggered by a new cycle of enhanced volatile supply due to carapace breaking and/or shallow magma intrusion (Martínez, 2008; Rymer et al., 2009). In recent years, fumarolic activity has been concentrated at the CPC, which has occasionally shown incandescence when gas temperatures rose above 600 °C in 2011, 2012 and 2014. Ongoing strong CPC degassing (at least until 2015), testifies a continuous supply of magmatic volatiles (Fischer et al., 2015; OVSICORI-UNA, http://www.ovsicori.una.ac.cr).

3. Sampling and analytical methods

3.1. Sampling techniques

Most of the samples from Laguna Caliente and fumarole condensates discussed here were routinely collected by OVSICORI-UNA (Observatorio Sismológico y Vulcanológico de Costa Rica, Universidad Nacional). The samples from Laguna Caliente were usually taken at a relatively easily accessible location on the eastern shore. The temperature and pH of the lake were directly recorded in the field with the aid of a thermocouple and a portable pH electrode, respectively. The water samples had been stored unfiltered and untreated in high density polyethylene (HDPE) bottles at room temperature (20–25 °C).

During our field campaign in April–May 2012, fumarole temperatures were measured with a thermocouple, and gas condensate samples were taken at vents were the flow was vigorous and constant. The condensates were collected using a glass condenser connected to a glass Dewar tube, which was in turn coupled to a titanium pipe. The samples were stored in 100 ml HDPE plastic bottles with air tight caps at room temperature. Older fumarole samples analysed also represent condensates that had been collected by OVSICORI-UNA in a similar way.

3.2. Analytical methods

3.2.1. Major anions

Because long storage times had occasionally resulted in the formation of precipitates in samples of hyperacid lake waters (mainly gypsum, anhydrite and amorphous silica) and fumarole condensates (elemental sulphur), all of the samples were filtered through a 0.2 μm pore-size cellulose acetate membrane prior to analysis. Measurements of pH, electrical conductivity (C) and redox potential (Eh) at the Department of Earth Sciences of Utrecht University were performed at 19 ± 1 °C using a WTW® 3430 portable multimeter. The pH electrode was calibrated with pH 1, 4 and 7 buffers, the conductivity electrode with a 0.01 M KCl standard, and the Eh electrode with a 420 mV buffer solution. The concentration of SO_4^{2-}, Cl^-, F^-, and Br^- were determined by ion chromatography (IC) at the Department of Earth Sciences of Utrecht University, using a Dionex® ICS-3000, equipped with a Dionex®IonPac® AS 19 column. A gradient elution of 10–50 mM KOH was utilized. The samples were diluted 10 to 300 times with deionized water (18.2 MΩ/cm) before analysis. Sulphate and Cl^- were determined with a precision of 1%, and F^- and Br^- with a precision of 2 and 5%, respectively. Major cations in crater lake waters (Na, K, Mg and Ca) and total sulphur (S_T) were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES), using a Spectro Ciros® instrument at the Department of Earth Sciences of Utrecht University. The samples were diluted 10 to 100 times and acidified with 2% Suprapur® HNO_3 acid. The analytical precision obtained from control samples was less than 3% for all of these elements.

3.2.2. Chlorine isotopes

Samples for $\delta^{37}Cl$ analysis were prepared and analysed following the procedure of Eggenkamp (1994). Ten milligrammes of AgCl was

precipitated by the addition of 0.2 M AgNO$_3$ to a specific amount of sample, which was determined by its chloride concentration. Before the formation of AgCl precipitate, the ionic strength of the sample was adjusted with 4 ml of 1 M KNO$_3$, and the pH was fixed to a value of 2.2 through the addition of 2 ml of a Na$_2$HPO$_4$-citric acid buffer. Next, the solution was heated to 80 °C and 1 ml of 0.2 M AgNO$_3$ was added. Since black precipitates of Ag$_2$S formed in fumarole condensates and some of the lake water samples due to the presence of H$_2$S$_{(aq)}$, the procedure was modified in order to completely oxidize the total sulphur to SO$_4^{2-}$. In these cases, samples were prepared with 4 ml of 1 M KNO$_3$, 1 ml of H$_2$O$_2$ (30 wt%), and 1 ml of concentrated HNO$_3$ (65%), and were then heated to 80 °C for 30 minutes before the 0.2 M AgNO$_3$ was added. The AgCl precipitates were filtered through a Whatman® type GF/F glass fibre filter and dried overnight at 80 °C. Subsequently, AgCl was reacted with iodomethane (CH$_3$I) in order to form chloromethane (CH$_3$Cl) at 70–80 °C during 48 h in vacuum glass ampoules. The chloromethane was separated from excess CH$_3$I by gas chromatography using a 75 cm long, 6.35 mm OD SS column, filled with Porapak® Q 80–100 mesh at 140 °C with helium as carrier gas. The analyses of CH$_3$Cl were carried out on a VG SIRA 24 EM mass spectrometer at the Department of Earth Sciences of Utrecht University. Chlorine isotope data are reported as a delta notation (δ^{37}Cl), in which the (^{37}Cl/^{35}Cl) isotope ratio of a sample is compared to a standard with a known (^{37}Cl/^{35}Cl) ratio, commonly taken to be the Standard Mean Ocean Chloride or SMOC (Kaufmann, 1984):

$$\delta^{37}Cl = \frac{\left(^{37}Cl/^{35}Cl\right)_{sample} - \left(^{37}Cl/^{35}Cl\right)_{SMOC}}{\left(^{37}Cl/^{35}Cl\right)_{SMOC}} \times 1000. \quad (1)$$

Given the constancy of the isotopic composition of ocean water (Kaufmann, 1984; Godon et al., 2004a; Liu et al., 2013) any sample of ocean water can serve as a standard with a δ^{37}Cl value of 0.00 ‰ versus SMOC. It is here represented by a sample of Atlantic ocean water collected near Madeira in 1982. The analytical precision was ±0.16‰ (1 σ), based on long-term analyses of this standard. As a rule, samples were analysed at least in duplicate. Reproducibility between duplicates was generally better than 0.1‰.

4. Results

4.1. Cl and Br concentrations in Laguna Caliente and CPC fumaroles

Concentrations of chloride and bromide as well as Br/Cl ratios in Laguna Caliente are shown in Fig. 3, together with the variations in lake volume, temperature and pH, recorded over almost four decades since the late 1970's. The time series for these parameters are based on the data presented here and the compilation of Martínez (2008). A representative subset is given in Table 1. In general, Cl and Br concentrations exhibit roughly similar changes with time. Their abundances were relatively high during Stages III and V when the activity was high. The maximum concentrations of Br and Cl were measured during Stage III, reaching 1820 mg/kg (23 mmol/kg) and 114,000 mg/kg (32 mmol/kg), respectively. Stage III, when temperatures were highest, was also marked by maximum Br/Cl molar ratios (up to 0.013), whereas they remained virtually constant at ~0.001 throughout Stage V, comparable to values observed in Stage II and at the beginning of Stage III (Fig. 3). It should be noted that Laguna Caliente was largely dry during most of Stage III and that samples from this period include those taken from isolated mud pools, which are therefore not necessarily representative for the lake system at large. Conversely, lowest Cl and Br concentrations were found during Substages IVA, IVC and IVE when the activity was weak, the lake water had cooled and pH values were relatively high. Measured concentrations were 4 mg/kg (0.05 mmol/kg) for Br and 10,200 mg/kg (288 mmol/kg) for Cl. This tendency of decreasing concentrations was
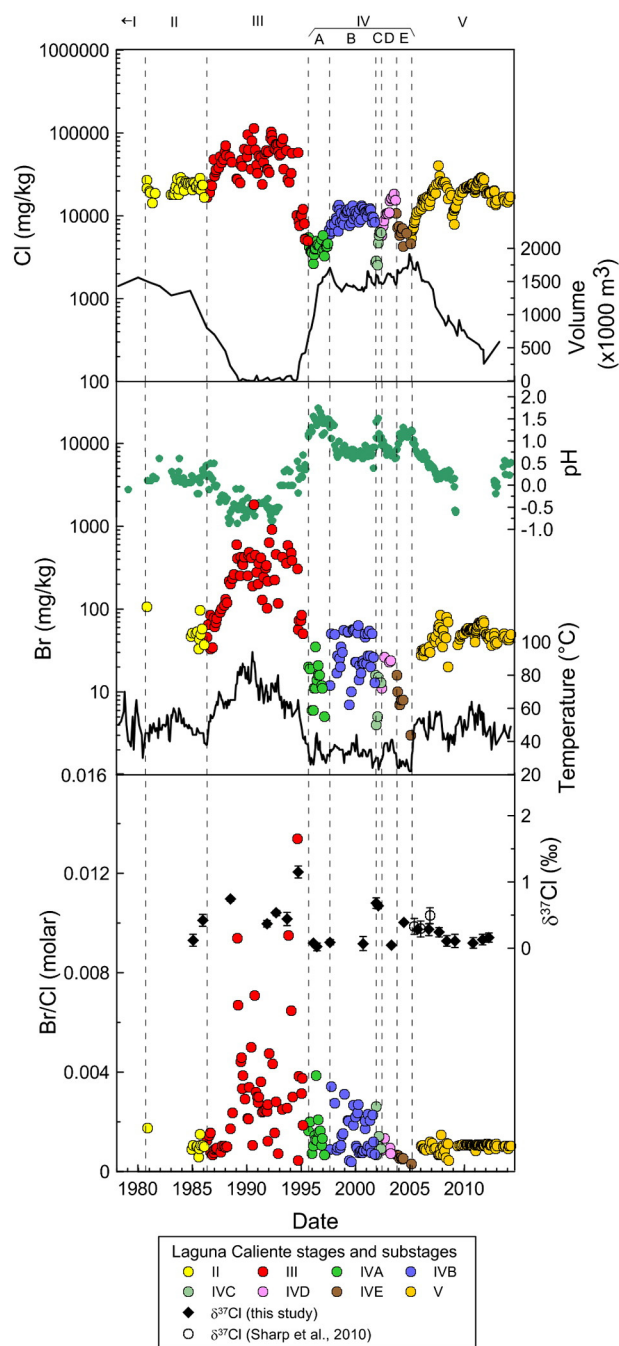
Fig. 3. Time series of Cl and Br concentrations, Br/Cl ratios, δ^{37}Cl values, lake volume, pH and temperature for Laguna Caliente. A trend of δ^{37}Cl composition with temperature is showed in Fig. 4.

enhanced by periods of high rainfall in 1995–1997 and 2003–2005 that further contributed to the dilution and volume increase of the lake. Also, Br/Cl ratios decreased considerably after Stage III, reaching minimum values during Substage IVE (Br/Cl molar ratio = 0.0003). During most of Stage IV (mid 1997-mid 2004), when the lake temperature was low (usually <40 °C), the Cl concentration in the lake exceeded that of SO$_4$, which is an uncommon feature for Laguna Caliente (Martínez, 2008).

The data set for Cl, Br and Br/Cl in the CPC fumarole condensates encompasses the period 2010–2012, within Stage V. The results are given in Table 2 and are illustrated in Fig. 5. Despite substantial fluctuations there is a tendency of decreasing Cl and Br concentrations, decreasing

Table 1

Chemical composition, physicochemical parameters and $\delta^{37}Cl$ values for selected samples from Laguna Caliente and Río Agrio hot spring, Poás volcano.

Date	$T_{sampling}$ (°C)	pH_{lab}	Cond. $_{lab}$ (mS/cm)	SO_4 (mg/kg)	S_T[a] (mg/kg)	Cl (mg/kg)	Br (mg/kg)	F (mg/kg)	Mg (mg/kg)	SO_4/Cl (mol/mol)	S_T/Cl (mol/mol)	Br/Cl (mol/mol)	F/Cl (mol/mol)	Mg/Cl (mol/mol)	$\delta^{37}Cl$ (‰)	Source
Stage II																
11/Jan./85	44	−0.21	324[b]	52,000	16,800	20,400	51	1120	640	0.94	0.91	0.0011	0.102	0.046	0.12 ± 0.09	(1,2)
29/Nov./85	45	0.30	390	62,700	21,000	23,400	57	1090	650	0.99	0.99	0.0011	0.087	0.040	0.42 ± 0.09	(1,2)
Stage III																
24/Jun./88	65	−0.61	n.d.	175,000	25,300	51,600	200	2970	990	1.25	0.54	0.0017	0.107	0.028	0.74 ± 0.03	(1,2,3)
1/Nov./91	70	−0.50	371	72,100	n.d.	61,100	330	6790	770	0.44	—	0.0024	0.207	0.018	0.37 ± 0.05	(1,2,4)
18/Sep./92	70	−0.60	n.d.	93,100	30,000	73,000	460	8390	1210	0.47	0.45	0.0028	0.214	0.024	0.53 ± 0.04	(1,2,5)
9/Sep./93	64	0.35	n.d.	50,400	18,100	61,400	350	5840	1280	0.30	0.33	0.0026	0.177	0.030	0.44 ± 0.10	(1,2,6)
23/Sep./94	65	−0.18	483	27,000	21,800	57,500	56	2660	610	0.17	0.42	0.0004	0.086	0.016	1.15 ± 0.09	(1,2,6)
Substage IVA																
23/Feb./96	26	1.55	n.d.	4480	n.d.	2630	6.1	140	n.d.	0.63	—	0.0010	0.100	—	0.08 ± 0.00	(1,2,6)
14/Jun./96	45	1.35	57	7000	4000	4960	14	330	480	0.52	0.89	0.0013	0.123	0.141	0.02 ± 0.06	(1,2,6)
Substage IVB																
5/Sep./97	35	1.30	n.d.	4060	2790	5960	12	170	480	0.25	0.52	0.0009	0.053	0.117	0.09 ± 0.04	(1,2,6)
12/Sep./00	35	0.60	106	9410	3630	12,700	24	620	520	0.27	0.32	0.0008	0.091	0.060	0.07 ± 0.11	(2,7)
Substage IVC																
27/Nov./01	30	1.07	56	3450	1260	2720	16	82	250	0.47	0.51	0.0026	0.056	0.134	0.68 ± 0.08	(2,7)
31/Jan./02	30	1.51	22	3590	1470	2540	5.0	52	230	0.52	0.64	0.0009	0.038	0.132	0.64 ± 0.04	(2,7)
Substage IVD																
30/Apr./03	41	0.67	134	10,500	5100	16,100	n.d.	620	430	0.24	0.35	—	0.072	0.039	0.05 ± 0.02	(2,7)
Substage IVE																
11/Jun./04	28	1.20	39	4540	1980	6480	b.d.l.	65	330	0.26	0.34	—	0.019	0.074	0.39 ± 0.01	(2,7)
Stage V																
20/Sep./05	52	0.70	123	12,800	6560	11,100	n.d.	750	360	0.43	0.65	—	0.126	0.047	0.28 ± 0.00	(2,7)
5/Oct./06	46	0.40	163	28,400	9410	16,700	n.d.	1140	620	0.63	0.62	—	0.127	0.054	0.28 ± 0.09	(2,7)
12/Sep./07	56	0.16	371	98,300	21,700	40,300	61	1800	730	0.90	0.60	0.0007	0.083	0.026	0.24 ± 0.07	(2,7)
4/Jun./08	42	0.16	323	75,200	18,500	31,300	80	1450	580	1.23	0.65	0.0011	0.086	0.027	0.11 ± 0.08	(2,8)
25/Feb./09	40	n.d.[b]	n.d.	n.d.	9830	11,500	n.d.	n.d.	290	—	—	—	—	—	0.11 ± 0.10	(2,8)
9/Nov./10	56	0.04[b]	498[b]	81,000	27,900	23,900	57	990	380	1.22	1.29	0.0011	0.077	0.023	0.08 ± 0.08	(1,2)
14/Sep./11	57	−0.06	587[b]	10,740	37,000	28,200	69	1150	410	1.39	1.45	0.0011	0.076	0.021	0.13 ± 0.08	(1,2)
18/Apr./12	47	−0.15	452[b]	92,400	27,200	21,800	43	1020	280	1.76	1.38	0.0009	0.087	0.019	0.16 ± 0.07	(1,2)
Río Agrio spring																
20/Jul./99	52	1.12	n.d.	15,700	4970	6210	11	150	850	0.93	0.89	0.0008	0.045	0.199	0.33 ± 0.09	(2,9)
14/Jun./00	52	1.45	n.d.	17,100	5660	6280	14	140	920	1.01	1.00	0.0010	0.042	0.213	0.23 ± 0.08	(2,9)
25/Oct./00	53	1.06	n.d.	16,600	5180	6300	14	135	850	0.97	0.91	0.0010	0.040	0.196	0.24 ± 0.02	(2,9)
29/Apr./02	51	1.07	n.d.	17,100	5880	6300	16	170	850	1.00	1.04	0.0011	0.050	0.198	0.23 ± 0.04	(2,9)

n.d.: not determined; b.l.d.: below detection limit.

Sources: (1) OVSICORI-UNA; (2) This study; (3) Rowe et al., 1992b; (4) Nicholson et al., 1992; (5) Nicholson et al., 1993; (6) Martínez et al., 2000; (7) Martínez, 2008; (8) Ayres, 2012, unpublished data; (9) Martínez, 1999, 2000, 2002, unpublished data.

[a] Total sulphur measured by ICP-OES.

[b] Measured at T = 19 ± 1 °C, whereas other samples were measured at T = 24 ± 2 °C.

Table 2
Chemical composition, physicochemical parameters and $\delta^{37}Cl$ values for gas condensate samples from the CPC fumaroles. Conductivity and pH were measured in the laboratory at T = 19 ± 1 °C. n.d.: not determined; b.l.d.: below detection limit.

Date	T sampling (°C)	pH lab	Cond. lab (mS/cm)	SO4 (mg/kg)	Cl (mg/kg)	Br (mg/kg)	F (mg/kg)	SO4/Cl (mol/mol)	Br/Cl (mol/mol)	F/Cl (mol/mol)	$\delta^{37}Cl$ (‰)
19/Jan./10	650	0.09	231	1180	21,900	51	72	0.020	0.00103	0.006	0.19 ± 0.03
23/Feb./10	640	0.00	272	900	26,500	52	100	0.013	0.00086	0.007	n.d.
7/Apr./10	566	2.02	2.47	2770	5440	6.3	100	0.188	0.00051	0.036	n.d.
21/May/10	148	0.91	35.4	2400	230	b.d.l.	7.9	3.780	—	0.063	n.d.
25/Jun./10	763	0.07	241	610	21,900	n.d.	80	0.010	—	0.007	−0.43 ± 0.09
16/Aug./10	650	0.14	212	280	19,800	36	43	0.005	0.00079	0.004	n.d.
8/Sep./10	760	0.09	231	650	21,400	14	14	0.011	0.00029	0.001	0.67 ± 0.01
22/Oct./10	590	0.58	73.8	2910	4220	8.0	130	0.255	0.00084	0.057	n.d.
9/Nov./10	595	0.60	148	3730	10,200	25	260	0.135	0.00105	0.048	1.52 ± 0.09
27/Jan./11	360	0.51	84	1260	7650	15	190	0.061	0.00086	0.047	1.73 ± 0.03
22/Feb./11	480	0.65	63.6	1700	3880	6.4	100	0.161	0.00073	0.050	7.37 ± 0.07
18/Mar./11	250	−0.27	465	68	47,000	78	86	0.001	0.00074	0.003	n.d.
15/Apr./11	250	0.09	216	860	19,600	25	19	0.016	0.00056	0.002	0.64 ± 0.08
27/May/11	280	0.12	216	600	20,100	25	5.9	0.011	0.00056	0.001	n.d.
22/Jul./11	760	0.10	213	1210	20,800	18	44	0.021	0.00038	0.004	−0.25 ± 0.10
13/Oct./11	186	1.05	22.7	990	930	1.8	75	0.393	0.00086	0.150	14.09 ± 0.08
27/Oct./11	114	0.84	23.2	3650	100	b.d.l.	31	12.9	—	0.556	n.d.
25/Jan./12	508	0.27	150	4270	12,280	25	n.d.	0.128	0.00089	—	n.d.
10/Feb./12	107	0.46	103	5480	39	b.d.l.	3.8	51.9	—	0.182	n.d.
24/Feb./12	107	1.14	18.2	1230	830	b.d.l.	6.4	0.544	—	0.014	13.48 ± 0.04
22/Mar./12	307	0.42	116	1570	2790	0.7	80	0.208	0.00016	0.053	n.d.
21/Apr./12	410	0.84	n.d.	1750	2600	4.5	73	0.246	0.00076	0.052	4.04 ± 0.05
8/May/12	238	0.63	n.d.	1400	3220	8.1	65	0.161	0.00112	0.038	n.d.
29/May/12	209	0.65	n.d.	6370	3350	6.8	169	0.702	0.00090	0.094	n.d.
20/Jul./12	301	0.84	n.d.	400	100	b.d.l.	30	14.3	—	0.534	n.d.

temperature and increasing pH with time. Peak concentrations of Cl and Br are 47,000 mg/kg (1326 mmol/kg) and 78 mg/kg (1 mmol/kg), respectively. The molar Br/Cl ratios exhibit some variation, but there is no obvious temporal trend. The majority of data scatter around 0.001, i.e. close to base line values found in the lake.

4.2. Cl isotope compositions of Laguna Caliente and CPC fumaroles

The $\delta^{37}Cl$ results for Laguna Caliente and CPC fumaroles (Tables 1 and 2) are shown in Figs. 3, 4 and 5. The values for the lake show minor fluctuations between +0.02 ± 0.06‰ and +0.74 ± 0.03‰. An
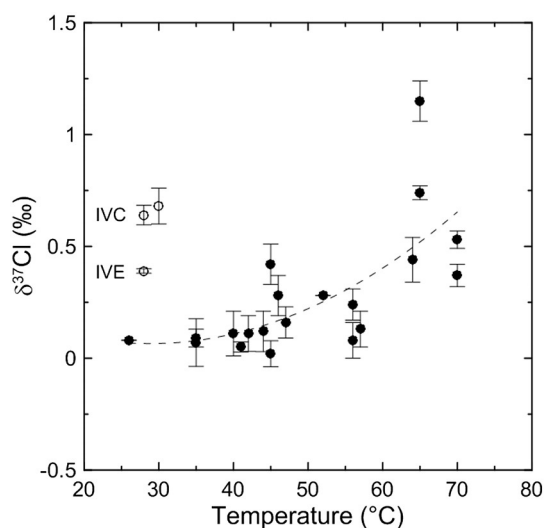

Fig. 4. Relationship between the $\delta^{37}Cl$ composition of Laguna Caliente water and temperature, illustrating increasing $\delta^{37}Cl$ at higher activity levels of the magmatic hydrothermal system. Note that the $\delta^{37}Cl$ values for low-activity substages IVC and IVE do not follow the trend, presumably because the entrance of brine water was temporarily blocked and volatile supply was restricted to gaseous input (cf. Martínez, 2008).

exceptional value of +1.15 ± 0.09‰ was found in one of the samples (September 1994) taken from pools when the lake had dried out. The $\delta^{37}Cl$ data can be ranked according to the Stages and Substages: III ≈ IVC–IVE > II ≈ V > IVA–IVB–IVD. Thus, the more active periods (II, III, and V) tend to be marked by higher $\delta^{37}Cl$ values than the most quiet one (IV), with the exception of Substages IVC and IVE. Data reported by Sharp et al. (2010) for samples taken in 2005 and 2006 are consistent with the slightly elevated values seen in our data for Stage V. As the time series of Fig. 3 illustrate, the modest rises in $\delta^{37}Cl$ during the active periods were associated with increased temperatures, halogen concentrations and acidity, relative to stage IV. Conversely, $\delta^{37}Cl$ values were also high during Substages IVC and IVE, when the lake was very quiet, temperatures low (ca. 30 °C) and pH relatively high (>1). Fig. 4 summarizes the relationship between $\delta^{37}Cl$ and temperature of Laguna Caliente and the exceptional conditions during Substages IVC and IVE.

In contrast to the modest range in the lake water, the CPC fumarole condensates display a large variation in $\delta^{37}Cl$, with a maximum of +14.09 ± 0.08‰ at the lowest gas temperatures (<200 °C) and a tendency of decreasing $\delta^{37}Cl$ values towards ca. 0‰ at the highest temperatures (>600 °C), although relatively low isotope ratios were also found in some samples when temperatures were around 300 °C (Fig. 5). Sharp et al. (2010) reported a comparable a large $\delta^{37}Cl$ range (from −1.3‰ to +18.75‰) in condensates and gas samples from low-temperature fumaroles (<160 °C) on the eastern terrace of the active crater (Main and Naranja fumaroles), which were collected in 2001 (Stage IV) and 2006–2007 (early Stage V) (Fig. 6).

5. Discussion

Fig. 7 compares Cl and Br contents of terrestrial reservoirs and bulk igneous rocks with fumarole gases and condensates from Poás and other subduction-related volcanoes. The Br/Cl molar ratios in most of these materials show little variation (mostly between 0.01 and 0.001) and the fractionation of these elements relative to chondritic values is modest. Fumarole condensates from arc volcanoes fall within this range but also include considerably lower values. Some of the variability in Br/Cl ratios among fumarole condensates might be attributable to a
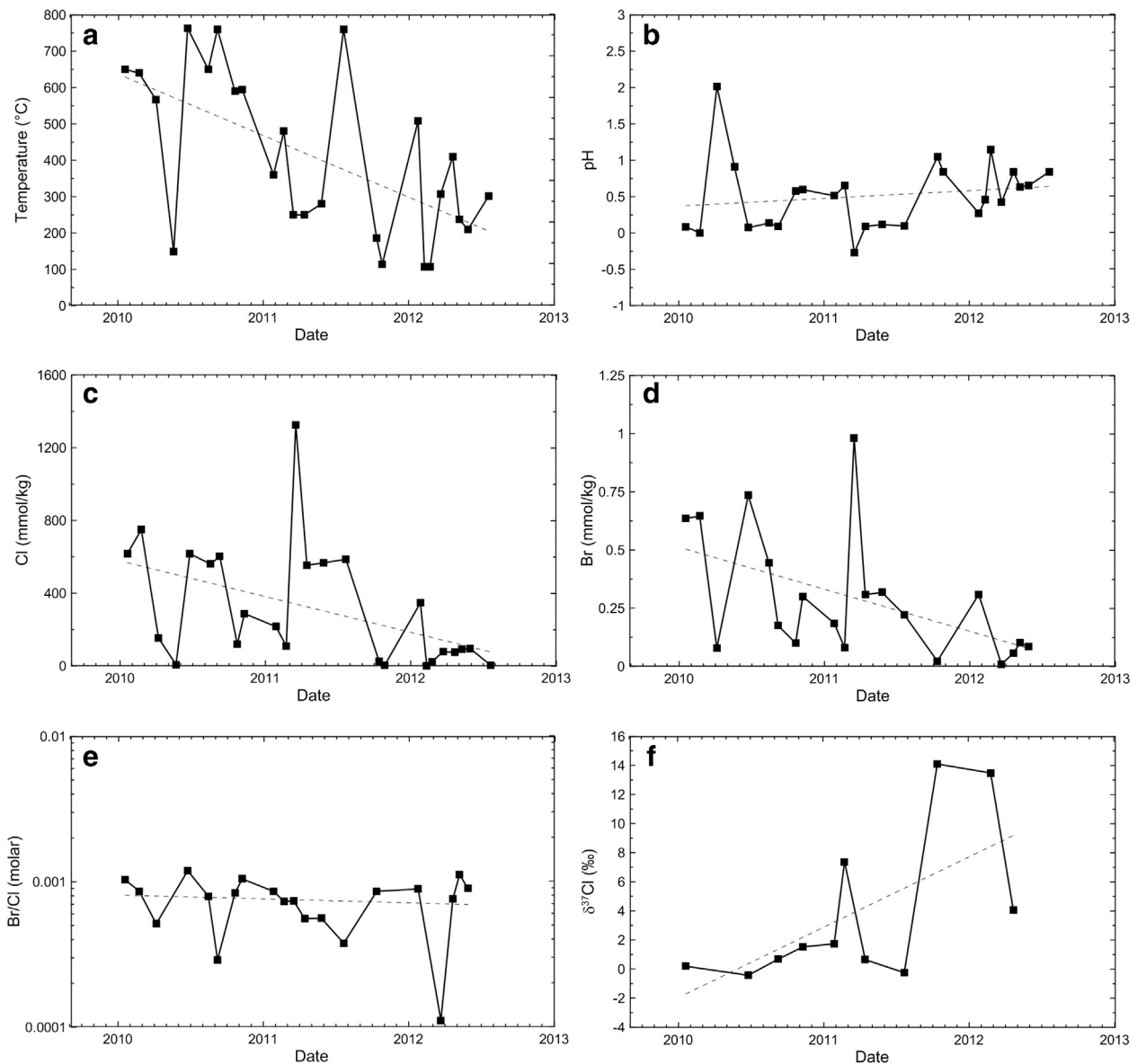
Fig. 5. Time series of temperature, pH, Cl, Br, Br/Cl ratios and $\delta^{37}Cl$ values for condensates from the CPC fumaroles. Hyphenated lines indicate generalized trends.

mantle source heterogeneity, considering the variation in pre-eruptive magmatic values and the usually conservative behaviour of these halogens during magma differentiation and degassing (Balcone-Boissard et al., 2010). It is conceivable that the mantle source range extends towards the low end of Br/Cl ratios (Fig. 7), since values lower than 0.00034 have been reported for condensates from high-temperature (T > 500 °C) fumaroles (e.g., Taran et al., 1995). Nevertheless, a shift towards lower values is not necessarily a primary feature but may also be the result of preferential partitioning among coexisting fluid phases in shallow volcanic environments.

Fig. 8 shows a compilation of $\delta^{37}Cl$ compositions of terrestrial materials. Values generally scatter around 0‰, indicating that chlorine isotopes do not fractionate significantly relative to Earth's ocean water. The mantle $\delta^{37}Cl$ composition is rather controversial since values from <− 3.0 to 0.0‰ have been proposed (Sharp et al., 2007, 2013; Bonifacie et al., 2008b; Layne et al., 2009). The most significant fractionation occurs at low temperatures, making isotope signatures useful tracers of near-surface processes (Barnes et al., 2009; Sharp et al., 2010; Li et al., 2015). The most negative values have been found in marine pore waters and formation waters (Eggenkamp, 1994; Eastoe et al., 1999). Fumarolic gases and

condensates from Poás and other volcanoes represent the opposite side of the range. They exhibit the most positive $\delta^{37}Cl$ values and the largest spread in the entire spectrum of terrestrial materials (Eggenkamp, 1994; Wahrenberger et al., 1997; Musashi and Eggenkamp, 2000; Barnes et al., 2008; Sharp et al., 2010; Rizzo et al., 2013). The following sections will discuss the possible origins of the observed temporal variations in Br/Cl ratios and $\delta^{37}Cl$ values observed in the lake water and fumarole condensates of Poás volcano. For both signatures, we will explore possible fractionation effects from magmatic processes, gas–liquid-solid interactions in shallow subsurface environments and from evaporation of the lake water body at the surface. Finally, we will discuss implications for volcano monitoring and surveillance.

5.1. Behaviour of halogens in magmas

Since chlorine and bromine have large ionic radii ($Cl^- = 181$ pm, $Br^- = 196$ pm), they cannot be easily accommodated into crystalline structures so that only a few minerals (e.g., sodalite and apatite group) are potential carriers of these elements. Therefore, both halogens tend to behave as incompatible elements in magmatic processes (Schilling
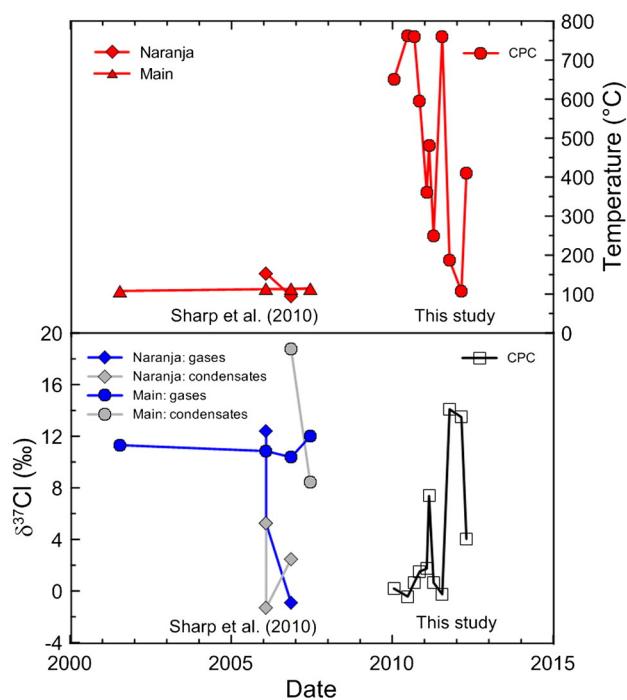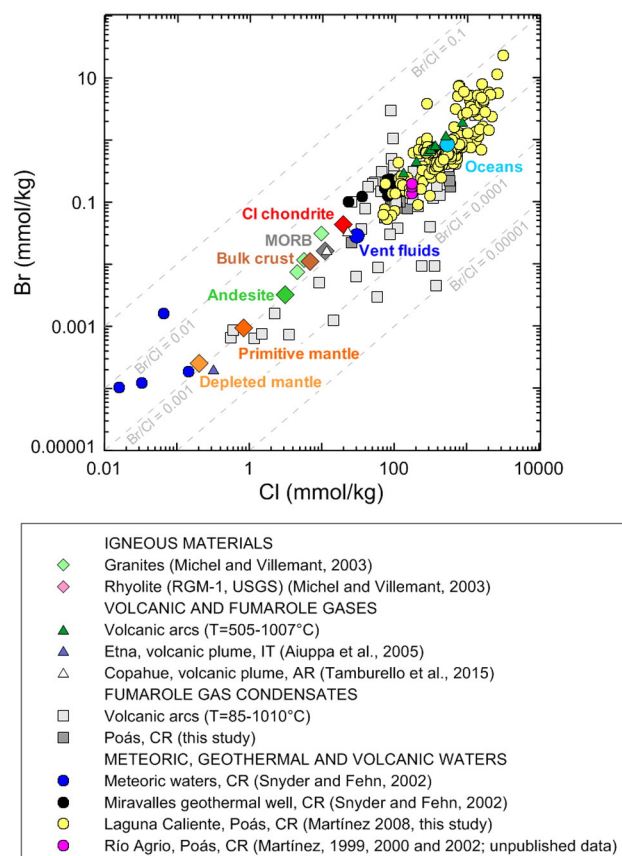
Fig. 6. Times series of fumarole temperatures and δ^{37}Cl values of condensates for the CPC fumaroles (this study) in comparison with data for the Naranja and Main fumaroles on the eastern side of the crater (Sharp et al., 2010). The error bars for δ^{37}Cl do not exceed the size of the symbols.


Fig. 7. Compilation of Cl and Br contents of igneous rocks, volcanic gases and condensates, meteoric, volcanic and geothermal waters, Cl chondrite and major terrestrial reservoirs. Data sources: Cl chondrite (Palme and Beer, 1993), primitive mantle (Palme and O'Neill, 2007), depleted mantle (Schilling et al., 1980), MORB (Shinonaga et al., 1994), bulk crust (Rudnick and Gao, 2003), andesite (reference material JA-2) (Shinonaga et al., 1994), granites (Michel and Villemant, 2003), rhyolite (reference material RGM-1) (Michel and Villemant, 2003), vent fluids (German and Von Damm, 2003), oceans (Bruland and Lohan, 2003), fumarole gases in volcanic arcs (Menyailov et al., 1986; Giggenbach, 1993; Shinohara et al., 1993; Symonds et al., 1996; Taran et al., 1995; Giggenbach, 1996; Hammouya et al., 1998), fumarole gas condensates in volcanic arcs (Gemmell, 1987; Symonds et al., 1987, 1990; Taran et al., 1995; Goff and McMurtry, 2000), Etna´s volcanic plume (Aiuppa et al., 2005), Copahue´s volcanic plume (Tamburello et al., 2015), meteoric, geothermal and volcanic waters (Snyder and Fehn, 2002; Martínez 2008; Martínez 1999, 2000 and 2002 [unpublished data]).

et al., 1980; Villemant and Boudon, 1999). Additionally, large Cl and Br fractionations cannot be generated as a consequence of low-pressure fractional crystallization or partial melting (Schilling et al., 1980). Conversely, substantial differences in Cl contents between lava blocks and pumice clasts at Soufrière Hills volcano illustrate that the interaction between groundwater vapours with a lava dome can control Cl and probably Br variations (Harford et al., 2003). Lowenstern et al. (2012) demonstrated that large amounts of halogens can be released during near-surface crystallization of rhyolitic lavas. Fluorine, on the other hand, has a distinct behaviour. Because of its much smaller ionic radius (F$^-$ = 133 pm), F is capable of substituting OH$^-$ groups into major rock forming minerals (Luth, 2003) and therefore is much less efficiently extracted from magmas during degassing processes, compared to Cl and Br (Villemant et al., 2003; Balcone-Boissard et al., 2010). As a result, ratios of F over other halogens in magmatic gases are relatively low and variable, and the F/Cl ratios of a melt tend to increase with halogen degassing (Villemant et al., 2003; Wang et al., 2014). Since chlorine and bromine are extracted with similar efficiency, they do not show a significant fractionation from melts at high pressures by H$_2$O-rich fluids exsolved from magmas or during slow effusive magma degassing (Balcone-Boissard et al., 2010). In summary, the incompatibility of halogens during magma degassing can be expressed as Cl $\approx$ Br > F (Pyle and Mather, 2009; Wang et al., 2014).

To the best of our knowledge, there are no Cl and Br data from bulk lavas or melt inclusions from Poás volcano, which implies that there are no constraints regarding original magmatic Br/Cl ratios. Given the restricted range in subduction related calc-alkaline magmas (molar Br/Cl ratios between 0.0007 and 0.004, Balcone-Boissard et al., 2010), it is reasonable to assume a ratio on the order of 0.001. Chlorine and bromine are exsolved from degassing magmas as HCl$_{(g)}$ and HBr$_{(g)}$, respectively (Aiuppa, 2009). The abundances of these compounds in magmatic gases remain virtually intact when the magmatic gases rise to the surface as long as there is no significant interaction with shallow hydrothermal systems or aquifers (Symonds and Reed, 1993). When gases interact with shallow, low temperature aqueous systems, the halogen acids will usually be completely dissolved owing to their high aqueous solubilities (Symonds et al.,

2001; Villemant et al., 2005), provided that the gas/water ratio is not excessively high and that the system is able to attain equilibrium. For these reasons, our discussion will be oriented to fractionation between Br and Cl in near-surface processes, starting from the assumption that the magmatic Br/Cl signature at Poás falls within the range of subduction-related high-temperature gases and condensates worldwide.

5.2. Br-Cl fractionation due to vapour–liquid phase separation

There is an ongoing debate on the fractionation mechanisms that affect Cl and Br during vapour–liquid phase separation. Fluids from submarine hot springs at mid-ocean ridges typically have Cl concentrations and Br/Cl ratios that depart significantly from seawater values. Bruland and Lohan (2003) report, for seawater, Cl = 546 mmol/kg, and Br/Cl = 0.00154 (molar). For instance, hydrothermal fluids from the East Pacific Rise (EPR) at 9–10°N have chlorine concentrations as low as 32.6 mmol/kg, while the lowest Br/Cl ratios (40% of seawater) were found in the low-salinity fluids (Oosting and Von Damm, 1996). Berndt and Seyfried (1990) suggested a combined effect of phase separation and halite precipitation or dissolution, since their experiments in the system NaCl–NaBr–H$_2$O could not explain the anomalous Br/Cl ratios values observed at mid-ocean ridges by simple subcritical phase
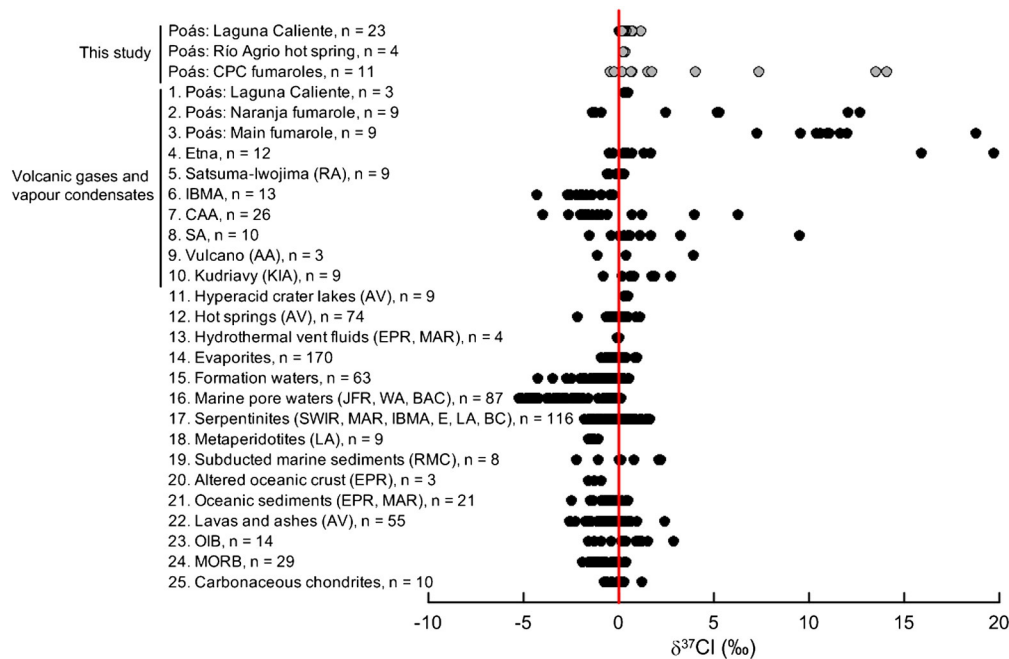
Fig. 8. Compilation of $\delta^{37}Cl$ data from solid and fluid materials from various geological settings. MORB = mid-ocean ridge basalts, OIB = oceanic island basalts, AV = volcanic arcs, EPR = East Pacific Rise, MAR = Mid-Atlantic Ridge, RMC = Raspas Metamorphic Complex, LA = Ligurian Alps, SWIR = Southwest Indian Ridge, IBMA = Izu-Bonin Mariana Arc, E = Elba island, BC = Beltic Cordillera, JFR = Juan de Fuga Ridge, WA = West Atlantic, BAC = Barbados Accretionary Complex, KIA = Kurile Islands Arc, AA = Aeolian Arc, SA = Sunda Arc, CAA = Central American Arc, RA = Ryukyu Arc. References: (1,2,3) Sharp et al., 2010; (4) Rizzo et al., 2013; (5) Musashi and Eggenkamp, 2000); (6) Barnes et al., 2008; (7) Sharp et al., 2010; (8) Eggenkamp, 1994; 9) Wahrenberger et al., 1997; (10) Wahrenberger et al., 1997; Sharp et al., 2010; (11) Eggenkamp, 1994; Sharp et al., 2010; Rodríguez, 2014, unpublished data; (12) Eggenkamp, 1994; Musashi et al., 2008; Sharp et al., 2010; Rodríguez, 2014, unpublished data; Li et al., 2015; (13) Bonifacie et al., 2005; (14) Eggenkamp, 1994; Eastoe et al., 1999, 2007; Sharp et al., 2007; (15) Eggenkamp, 1994); Eastoe et al. (1999); (16) Hesse et al., 2000; Godon et al., 2004b; Bonifacie et al., 2007; (17) Barnes and Sharp, 2006; Barnes et al., 2006, Barnes et al., 2008; Bonifacie et al., 2008b; John et al., 2010; (18) Bonifacie et al., 2008b; (19) John et al., 2010; (20) Bonifacie et al., 2007; (21,22) Barnes et al., 2008, 2009; (23) John et al., 2010; (24) Bonifacie et al., 2008a; Sharp et al., 2007; (25) Sharp et al., 2013. The error bars for $\delta^{37}Cl$ do not exceed the size of the symbols.

separation alone. On the other hand, fluid inclusions in sphalerite with Br/Cl ratios higher than twice that of seawater from the JADE field (Central Okinawa Trough, Japan) indicated a stronger effect of phase separation on Br/Cl ratios than predicted by experimental data. Halite precipitation could also produce high Br/Cl ratios but the observed co-variation with a significant $\delta^{37}Cl$ range argues against this explanation in view of the very little Cl isotopic fractionation between brine and halite (Lüders et al., 2002). Koschinsky et al. (2008) also reported relatively high Br/Cl ratios for hydrothermal vent fluids produced under subcritical or supercritical phase separation conditions at 5°S on the Mid-Atlantic Ridge. Liebscher et al. (2006) found a preferential partitioning of Br into the liquid in their experiments at 380–450 °C and 229–417 bars. In contrast to the closed-system conditions of the experiments mentioned above, Foustoukos and Seyfried (2007) determined values for Br and Cl partitioning between vapour, brine and halite under extreme phase separation conditions using an open-system approach in a flow-through reactor (388–550 °C, 244–351 bars, $pH_{25°C,1\ bar}$ = 3.5–6.9). Their results indicated a preferential partitioning of Br into the vapour phase. Considering this available evidence, the fractionation of Br and Cl due to phase separation is inconclusive. A significant difference between the experiments indicating a preferential Br uptake by the vapour (Berndt and Seyfried, 1990, 1997; Foustoukos and Seyfried, 2007) and the ones favouring a stronger partitioning into the liquid (Liebscher et al., 2006) is that the former were carried out in a more complex system than NaCl–NaBr-H_2O, containing additional components such as K, Ca, Li, Sr, Rb, B and Ba. We assume that results from such more complex systems are more applicable to the hyperacid brines of Poás volcano, given their elevated concentrations of dissolved rock forming elements.

5.3. Br-Cl fractionation due to mineral precipitation

Precipitation of halite is a potential mechanism to fractionate halogens, with Br tending to remain in the fluid and Cl fractionating in the solid (Stoessell and Carpenter, 1986; Siemann and Schramm, 2000). However, even during Stage III when Cl and Br concentrations were the highest, they remained well below the saturation levels for halite, consistent with the absence of chloride precipitates in Laguna Caliente. Only potassium-bearing halite ($K_{0.2}Na_{0.8}Cl$) has been found as a minor phase in sediments around the lake, presumably an evaporation product of acid brines expulsed from the lake during phreatic explosions. In view of its rarity and the intense rain fall in the summit area of Poás volcano, its existence will be transient and insignificant for any effective Cl–Br fractionation in the lake water. Zhao et al. (2014) found experimentally that jarosite [$KFe_3(SO_4)_2(OH)_6$] can incorporate halogens when it precipitates from a Cl- and Br-bearing aqueous solution, and that the remaining solution becomes more depleted in Br due to preferential uptake of this anion by the mineral. Jarosite has been found on rock surfaces in the surroundings of Laguna Caliente as alteration product of basaltic andesites and acid rain or brine spray. Because of its inconspicuous abundance and absence of detectable Cl or Br in EPMA results, we discard a role of jarosite in controlling Cl/Br ratios in the lake water. Among the minerals that will be stable in the deeper and hotter parts of volcanic–hydrothermal system at Poás, alunite [$KAl_3(SO_4)_2(OH)_6$] could have an effect on Br/Cl in associated brine water assuming if it would have a similar preference for Br compared to jarosite. Since precipitation and re-dissolution of alunite has an influence on the chemistry of the lake water (Martínez, 2008), a role in the fractionation of Br and Cl is conceivable. In any case, further work is needed to test this hypothesis. Other halogen-bearing minerals that can potentially fractionate Br from Cl during their formation include amphiboles, scapolite and Fe-Mg hydroxyl-chlorides, as has been advocated for oceanic crust environments (Seyfried et al., 1986; Campbell and Edmond, 1989). In the absence of evidence for their presence in the subsurface of Poás, we consider a role of these minerals unlikely. In the following sections, the effect of phase separation and mixing of deep gases with shallow aquifers on Br-Cl fractionation will be discussed.

5.4. Br/Cl ratios in Laguna Caliente

Once the magmatic gases $HCl_{(g)}$ and $HBr_{(g)}$ reach a water body (lake or a subsurface aquifer), they dissociate into the correspondent anions Cl^- and Br^- according to the reactions:

$$HCl_{(g)} = HCl_{(aq)} \tag{2}$$

$$HCl_{(aq)} + H_2O = H_3O^+ + Cl^- \tag{3}$$

$$HBr_{(g)} = HBr_{(aq)} \tag{4}$$

$$HBr_{(aq)} + H_2O = H_3O^+ + Br^-. \tag{5}$$

Considering the difference in the acid dissociation constants for reactions (3) and (5) at 25 °C (log K equals 0.51 and 8.60, respectively; Johnson and Pytkowicz, 1978; Pokrovskii, 1999), $HBr_{(aq)}$ is a stronger acid and dissociates even more readily than $HCl_{(aq)}$ (Myers, 1976) if the system is able to attain equilibrium. In cases of extreme acidy, the equilibrium shift towards the left hand side of the equations and will promote the formation of both $HCl_{(g)}$ and $HBr_{(g)}$. Therefore, given this dissociation difference between the acids, $HCl_{(g)}$ could form and escape preferentially from acid brines under circumstances of decreasing pH, leaving a relative Br-enriched solution. Evaporation of HCl fumes from Laguna Caliente occurs during periods of high activity and extremely low pH (Rowe et al., 1992a, 1992b; Martínez, 2008; Rouwet and Ohba, 2015). Rouwet et al. (2016) used a mass balance approach to estimate the Cl concentration in the evaporation plume at 13,300 mg/l for the period 2005–2010, i.e. during the initial years of the active Stage V. This value falls in the range of Cl concentrations measured in the CPC fumarole condensates (Table 2). Hence, the increased Br/Cl ratios in the lake during the highly active Stage III could, at least partly, be associated with evaporative loss of $HCl_{(g)}$. It must be noted that many of the high Br/Cl values for Stage III are from samples taken when the lake had dried out, and represent small-volume hot pools that were more susceptible to evaporation effects. An alternative explanation is that the elevated Br/Cl ratios observed during active periods had a deep origin and were created in a two-phase zone above the chilled margin of the magma body. Commonly, this will be a vapour-dominated zone in the deeper parts and a liquid-dominated one at shallower depths (Rowe et al., 1992a), but shifts in the gas/liquid proportions in response to changes in the rate of magmatic degassing, temperature or open/closed system conditions are to be expected. We explore the subsurface behaviour of the halogens using enthalpy vs. Cl and Br diagrams, which predict the concentrations in a deep fluid reservoir and the coexistence of vapour and liquid (Arnórsson, 2000), and calculate Br/Cl ratios for both phases based on vapour–liquid distribution coefficients from Berndt and Seyfried (1990). Reservoir temperatures required to compute the enthalpy and steam fraction are estimated by the Na-K geothermometer from Arnórsson et al. (1998), which is considered more reliable than SiO_2 or Na–K–Ca geothermometers in view of the abundant precipitation of amorphous silica and gypsum in the lake. Even though the temperatures calculated for the deep aquifer fluids (T = 225–456 °C) should be taken as crude approximations only, since the acid nature of the fluids questions an equilibrium with alkali feldspars on which the calibration of the Na-K geothermometer is based, these inferred temperatures exhibit similar trends compared to the measured surface temperatures of Laguna Caliente waters. The cold end-members of this plot are represented by the meteoric waters of Botos Lake (Snyder and Fehn, 2002) and hot springs on the eastern and north-eastern terraces of Laguna Caliente that were active from 1999 till 2006 (Martínez, 2008). Additionally, samples from Río Agrio hot spring water were included, which is assumed to correspond to the acid brine circulating through deeper parts of Poás volcanic system (Table 1). According to the enthalpy vs. Cl and Br diagrams (Fig. 9) most of the water compositions from Stage III and V show an enthalpy excess, which can be explained by the presence of steam-rich fluids.

Conversely, dominant processes during Stage II and IV were evaporation or steam loss and mixing with meteoric waters. Based on the concentrations inferred for the deep reservoir (Fig. 9), the approximate Br/Cl molar ratio of the magmatic component (i.e., parent fluid before boiling, evaporation and mixing with meteoric waters) is ca. 0.0016, close to the arc-type magmatic signature expected for Poás (see Section 5.1). Calculated Br/Cl ratios are higher for the steam than for the liquid phase during Stages III and V (Fig. 10) when the lake was extremely active. Increased Br/Cl ratios in the lake can thus be anticipated if gaseous input predominates over liquid influx, i.e., at high gas/liquid ratios that will be promoted when the magmatic hydrothermal system is hot. The observed elevated Br/Cl ratios in the lake and pool waters during Stage III are consistent with this scenario. The eventual drying out of the lake is in line with a prevalent supply of volatiles in gaseous form and with an intense evaporation, both leading to increased Br/Cl ratios. Although Stage V samples also exhibit an enthalpy excess, indicating an increased gas/liquid ratio during the renewed phreatic activity, the absence of a rise in Br/Cl suggests that halogen input via liquid water was still sufficiently large to avoid a significant deviation from magmatic values as seen during Stage III. This supposition is supported by the observation that the lake did not disappear during Stage V despite its volume reduction.

5.5. Br/Cl ratios in the CPC fumaroles

Molar Br/Cl ratios in the CPC fumaroles are considerably more uniform than those of the lake and do not show a systematic change with time (Fig. 5). Absence of clear correlations with temperature, pH, $\delta^{37}Cl$ or other chemical parameters suggests that the original Br/Cl ratio of fumarolic gas is largely preserved, despite the tendency for a progressive loss of both halogens through absorption by water. The average molar Br/Cl ratio of 0.0008 ± 0.0003 falls within the range of fumarolic values for arc volcanoes (Fig. 7) and compares reasonably well with the value of ca. 0.0016 inferred above for the magmatic component, taking the uncertainties into account. As will be discussed below, the chlorine isotope data of the condensates show stronger fluctuations and seem more susceptible to gas-water interaction than the Br/Cl ratios.

5.6. Chlorine isotopes in magmatic systems

Arc-related magmatism is expected to have slightly negative $\delta^{37}Cl$ values considering the common contribution of subducted components (marine sediments and altered oceanic crust) to sub-arc mantle sources (Straub and Layne, 2003; Sun et al., 2007; Bonifacie et al., 2008a; Pyle and Mather, 2009; John et al., 2010). Nonetheless, there is considerable overlap between $\delta^{37}Cl$ data reported for arc volcanics and MORB. Theoretical calculations and experiments indicate that chlorine isotope fractionation between minerals, melts and fluids at high temperatures (>400 °C) is insignificant (Schauble et al., 2003; Liebscher et al., 2006; Czarnacki and Halas, 2012), since chlorine is incompatible and does not experience speciation changes during melting and crystallization processes (Richet et al., 1977; Schilling et al., 1980). Consequently, chlorine isotope fractionation during partial melting, magma degassing, hydrothermal alteration and weathering is minimal so that the isotopic composition of the source material will be largely preserved (Bonifacie et al., 2007, 2008a; Barnes et al., 2008; Rizzo et al., 2013), with the possible exception when sorption processes in low-temperature aqueous environments play a role (Musashi et al., 2007).

5.7. Chlorine isotope fractionation effects in Laguna Caliente

The overall $\delta^{37}Cl$ signature of the lake water is similar to data from other hyperacid crater lakes (Fig. 8). The slightly positive values are equal to those of the high temperature gas condensates of the CPC fumaroles and fall in the range of island-arc volcanics (Figs. 4 and 8), which suggests that the Cl isotope composition of Poás lake water is close to that of the local magmatic gas. Input into the lake occurs directly
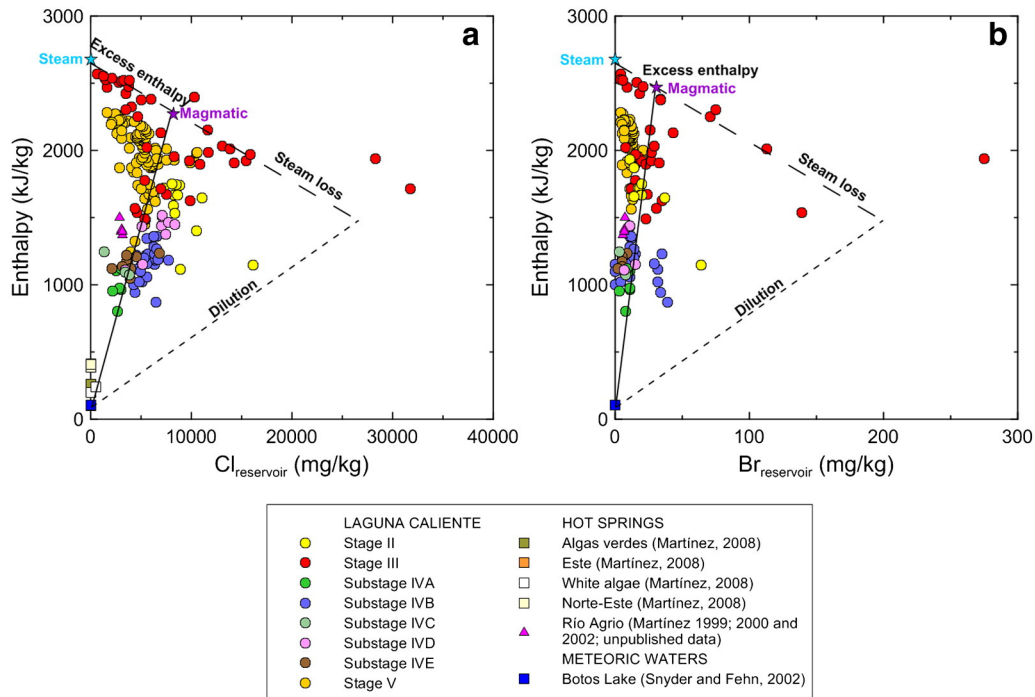
Fig. 9. Enthalpy vs. Cl and Br diagrams for Laguna Caliente samples, hot springs within and outside (Río Agrio spring) the active crater and meteoric waters represented by Botos Lake.

via subaqueous fumaroles or through influx of brine from a subsurface water body that had interacted with high-temperature gases. The $\delta^{37}Cl$ variation in the lake water may either reflect changes in the input signature or be a result of fractionation accompanying loss of Cl from the lake. In experiments with concentrated hydrochloric acid, Sharp et al. (2010) found that evaporation resulted in a $\delta^{37}Cl$ increase in the remaining acid, since the escaping hydrogen chloride was preferentially enriched in ^{35}Cl. Evaporation of $HCl_{(g)}$, which is a relatively

common feature for hyperacid lakes (Rouwet and Ohba, 2015; Capaccioni et al., 2016), is thus expected to enrich the Laguna Caliente water in the heavier ^{37}Cl isotope. When ignoring the data for Substages IVC and IVE (see below), $\delta^{37}Cl$ tends to correlate positively with temperature (cf., Fig. 4), which would hint at an evaporation effect, since HCl fumes have been noticed during periods when the lake temperature was high, and an evaporative loss of HCl has been predicted from a combined mass and Cl balance for a period overlapping Stage V (Rouwet et al., 2016). Still, evaporation effects on the $\delta^{37}Cl$ composition of the lake water will be minor and difficult to substantiate, given the large size of the dissolved Cl reservoir relative to the presumed evaporated amount, and the continuous supply of fresh brine and gas at the lake bottom. A significant chlorine isotope shift in the lake water due to evaporation may have been restricted to parts of Stage III when data represent isolated hot pools rather than a sizeable lake. Alternatively, the $\delta^{37}Cl$ variability of Laguna Caliente reflects temporal fluctuations in the mode of activity associated with magmatic volatile supply and/or changes in the gas–liquid ratio of the input. Increases in $\delta^{37}Cl$ that coincide with elevated chloride concentrations and temperature indicate that excess input of volatiles and heat into the lake produces a relative increase in heavy ^{37}Cl, presumably induced by the gas phase, in agreement with the frequent occurrence of phreatic eruptions during the active stages III and V. The alleged ^{37}Cl-enrichment is conceivable if pristine magmatic gas experienced scavenging before entering the lake water, and gaseous input was in excess relative to bulk supply through the combined input of gas and brine water.

In contrast, we attribute the relatively elevated $\delta^{37}Cl$ during the quiet Substages IVC and IVE to specific conditions in volatile transport. The low activity, reduced temperature and increased pH suggest that subsurface conduits were largely clogged (Martínez, 2008). Consequently, halogen supply was restricted to input of low-temperature gas and not (or much less) via influx of brine water. The data from the subaerial fumaroles on the CPC and eastern terraces (this work and Sharp et al., 2010) indicate that this low-temperature gas would have a high $\delta^{37}Cl$ signature (Fig. 6).


Fig. 10. Calculated Br/Cl molar ratios for steam and liquid fractions for Laguna Caliente and Río Agrio spring, based on the relationships between enthalpy and halogen contents inferred for the deep reservoir (cf. Fig. 8) and the vapour–liquid distribution coefficients of Berndt and Seyfried (1990) operating during phase separation at depth. See texts for further explanation. The legend is the same as in Fig. 8.

5.8. Chlorine isotope fractionation in the CPC fumaroles

A similar large range and strongly positive $\delta^{37}Cl$ values as observed in the CPC fumaroles also marked the Main and Naranja fumaroles on the eastern terrace (Sharp et al., 2010) that were active during Stage IV and the early years of Stage V, indicating that the CPC data are representative for tracing sources and processes governing the behaviour of halogens at Poás (Fig. 6). The extreme $\delta^{37}Cl$ values at the high end of the range are uncommon but are not unique to Poás. For instance, strongly elevated $\delta^{37}Cl$ values in gas and condensates up to $+9.47 \pm 0.37‰$, $+19.7 \pm 0.2‰$ and $+6.39 \pm 0.12‰$ have also been found at Lewotolo, Indonesia (Eggenkamp, 1994), Etna, Italy (Rizzo et al., 2013) and Santa Ana, El Salvador (Sharp et al., 2010), respectively (Fig. 8).

According to experimental work and theoretical approaches, the equilibrium chlorine isotope fractionation between HCl gas and dissolved Cl^- in an associated aqueous solution is modest, reaching a maximum of ca. 1.5‰ between 50 and 100 °C, with the gas phase being preferentially enriched in ^{37}Cl (Schauble et al., 2003; Sharp et al., 2010). The large $\delta^{37}Cl$ range in our fumarole samples and values up to $+14.09 \pm 0.08‰$ are therefore difficult to explain with simple equilibrium fractionation in a gas–liquid system. Furthermore, because the magmatic $\delta^{37}Cl$ signature is expected to be close to zero or slightly negative, mixing with another Cl source can be ruled out to explain the trend, as there are no know terrestrial reservoirs with a sufficiently positive signature to generate $\delta^{37}Cl$ values up to $+15‰$ or more. Since our data were obtained on condensates and not on samples of the entire fumarolic gas, a sampling bias is conceivable. However, $\delta^{37}Cl$ data on condensate and gas samples, collected from the east flank fumaroles at Poás on the same day (Sharp et al., 2010), provide no evidence for a systematic shift, as the isotopic compositions of condensates were equal, lower or

higher than those obtained in the corresponding gases. The behaviour suggests that results from condensates approximate the signatures of bulk fumarolic gas as long as the entire Cl budget is captured during sampling. The $\delta^{37}Cl$ range must therefore be attributed to an alternative fractionation mechanism.

The inverse relationship between $\delta^{37}Cl$ and sampling temperature in the CPC data, together with the temperature decrease from 763 to 107 °C between 2010 and 2012, favour a gradual change in the behaviour of the fumarole system over a period of approximately 2.5 years (Fig. 5). Also, when combining the CPC data with those of the 2001–2007 fumaroles with relatively low temperatures (95 to 153 °C) on the eastern flank (Sharp et al., 2010), it appears that the spread in $\delta^{37}Cl$ increases with decreasing temperature (Fig. 6). We attribute these tendencies to a transition from freely degassing magma with a near-primary $\delta^{37}Cl$ signature in a relatively dry pathway to a stronger interaction with more abundant water present in the shallow subsurface that created the ^{37}Cl-enrichment. Based on the results of flow-through experiments, Sharp et al. (2010) explained the high $\delta^{37}Cl$ values by a distillation process whereby recondensation of fumarolic gases on the conduit walls preferentially strips ^{35}Cl from the vapour. The authors argue that the liquid water on the wall must be continuously refreshed and dripping back in order to take up the large proportion of Cl required to create the high $\delta^{37}Cl$ in the remaining vapour. The time series for our CPC condensate samples also favours a preferential removal of ^{35}Cl by water but seems difficult to reconcile with a conduit-wall control alone, given the change in the fractionation magnitude with time. Instead, we attribute the temporal $\delta^{37}Cl$ increase in the CPC fumarole to an increase in the water/gas ratio during subsurface interaction with a water-rich body, which was promoted either by a decrease in the rate of magmatic degassing or by a larger supply of cool (meteoric) groundwater to a shallow aquifer. The
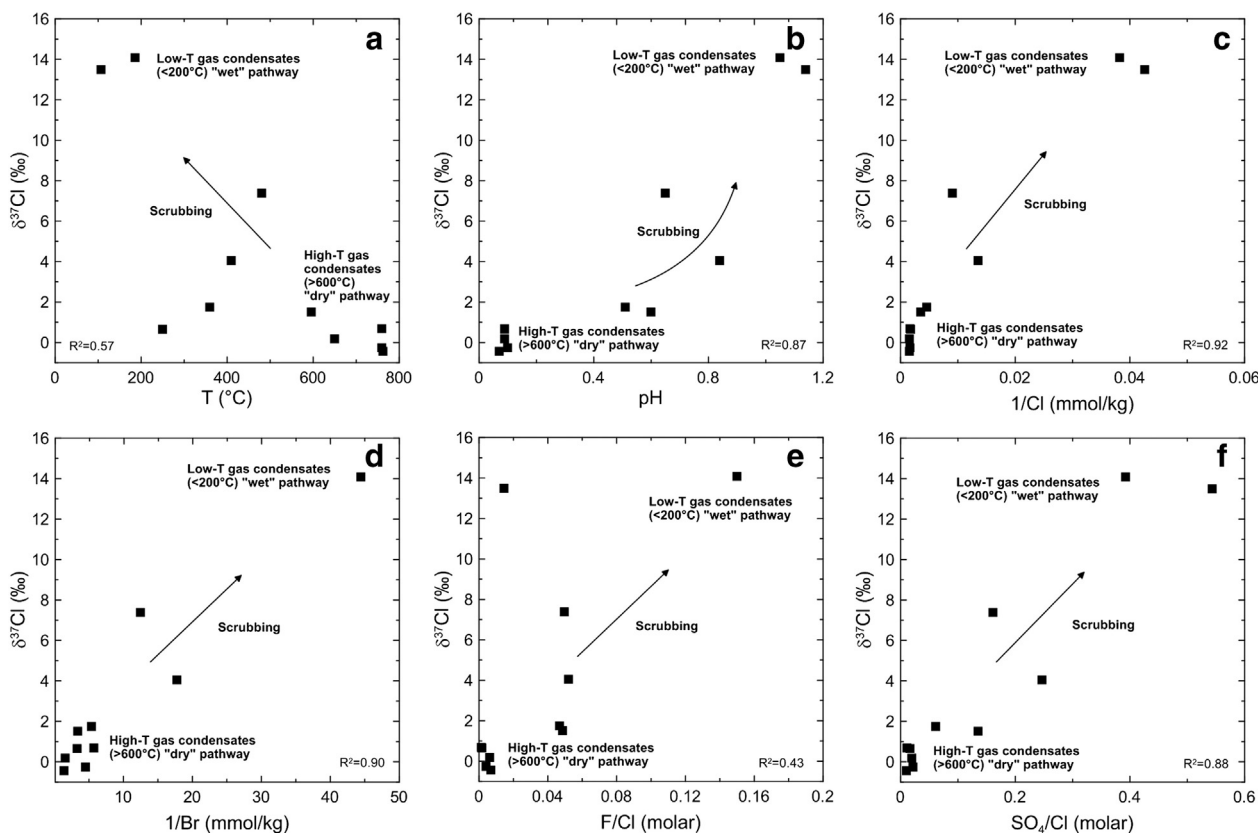
Fig. 11. Relationships between $\delta^{37}Cl$ and temperature, pH, 1/Cl, 1/Br, F/Cl and SO_4/Cl for CPC fumarole condensates, showing the effects of scrubbing. Increasing water/gas ratios during subsurface interaction correspond to a shift from a "dry" to a "wet" pathway. The $\delta^{37}Cl$ error bars do not exceed the size of the symbols.

roughly decreasing Cl and Br concentrations, decreasing temperature and increasing pH (Fig. 11), together with the correlations between $\delta^{37}Cl$ and temperature ($R^2 = 0.57$) and $1/Cl$ ($R^2 = 0.92$) and $1/Br$ ($R^2 = 0.90$) are consistent with more scavenging and thus support this scenario. Musashi and Eggenkamp (2000) observed an opposite trend in fumarolic gases from Satsuma-Iwojima, i.e. an increase in $\delta^{37}Cl$ values with temperature, and suggested a possible influence of marine water in the low temperature samples, whereas the high temperature gas would have better preserved the isotopic composition of the magma source. A marine influence is unlikely for the CPC fumarole signatures, given Poás position in the Central Cordillera, away from any coast.

5.9. Halogen ratios and $\delta^{37}Cl$: implications for volcano monitoring at Poás

The temporal evolution of halogen concentrations in hydrothermal springs and fumaroles is a potential indicator of subsurface magmatic activity (Ohba et al., 1994; Villemant et al., 2005, 2014; Aiuppa et al., 2009). However, concentration changes do not necessarily signal magma degassing, since they can also be controlled by non-magmatic processes such as evaporation, condensation, interaction with halogen-bearing lithologies, minerals or both deep and surface fluids. Chlorine isotopes may be more adequate if the Cl budget in spring water or fluids is a mixture of a magmatic contribution and one or more sources of shallow, non-magmatic origin (e.g., groundwater or seawater), and if their respective $\delta^{37}Cl$ signatures are sufficiently constrained. For example, Li et al. (2015) used a difference between local magmatic fluid ($-0.65‰$) and meteoric and seawater Cl (ca. 0‰) to test the applicability of $\delta^{37}Cl$ in thermal springs as monitor of the levels of magmatic Cl in the shallow hydrothermal systems of La Soufrière (Guadeloupe) and Montagne Pelée (Martinique). They inferred that magmatic Cl has a relatively short residence time of <30–80 years in arc volcanic springs and that Cl isotopes are particularly useful for monitoring systems that are infrequently active at centennial scale. Villemant et al. (2005) found that the halogen concentrations of the thermal spring waters of La Soufrière provide a record of magmatic degassing pulses that are delayed as a function of distance to the source. They associated intermittent Cl injections with the shallow intrusion of a magma body, invoking decompression-induced degassing during magma emplacement and a subsequent step degassing regime controlled by magma cooling and crystallization that lasted ca. 15 years since the seismo-volcanic crisis of 1976–1977. Renewed seismic activity in 1992, marking the onset of increasing gas flux and possibly recording the emplacement of fresh magma, ultimately resulted in increase in Cl in only one of the springs ca. a decade later (Villemant et al., 2014).

Our findings at Poás volcano further demonstrate that active processes in a vapour liquid system between intruded magma and the surface can be monitored if the compositions of lake water and fumaroles (Cl, Br concentrations, Br/Cl ratios and $\delta^{37}Cl$) are recorded over longer periods of time. Rises in Cl and Br contents in Laguna Caliente usually signal an increased supply of these volatiles from the magma source, either due to a new intrusion or by opening up new pathways, for example when volatiles pass freshly formed cracks in a solidified envelope of an earlier emplaced magma batch. Elevated Cl and Br contents in Laguna Caliente during Stage III and V indicate that this has repeatedly happened in the last decades. In both cases, an initial rise in Cl and Br concentrations (Fig. 3), as well as in F, SO_4 and polythionates (Martínez, 2008), accompanied by an increasing temperature and decreasing pH, preceded the onset of a period of phreatic eruptions of the lake. The Br/Cl ratios in Laguna Caliente may largely reflect the proportion of gaseous versus liquid-water input derived from the two-phase subsurface system. The relatively low Br/Cl ratios during Stage V are close to magmatic values, which points to bulk volatile supply from both gas and liquid without significant fractionation. The contrasting high Br/Cl ratios of Stage III are mainly from isolated pool waters sampled when the lake had dried out, and may therefore not be representative for the system at large. However, in the first years when the lake was still intact and its volume decreased,

a gradual increase in Br/Cl accompanied the concentration increase of both halogens (Fig. 3). We attribute this apparent Br excess to a predominance of gaseous over liquid input into the lake, whereby vapour was derived from boiling (phase separation) at depth. Interestingly, the Cl concentrations in the lake water started to decline earlier than Br (Fig. 3), marking the onset of HCl evaporation when the pH had reached sufficiently low values (see Section 5.4). Monitoring the $\delta^{37}Cl$ values in the lake provides information on the mode of volatile supply (gas versus liquid input) and on the relative proportions of interacting gas and water in the hydrothermal system where the magmatic volatiles are processed.

Sensible interpretations of the Cl isotope signals can only be achieved in combination with other monitored parameters. Base line values will be low (close to 0‰), which will be the case when the original magmatic signature is entirely transferred to the lake through the combined supply of gas and liquid from the hydrothermal system. A rise in the lake's $\delta^{37}Cl$ values is likely to record an excess input of gas that is previously enriched in ^{37}Cl during interaction with water within the edifice. This may occur during periods of high activity as well as during extremely quiet intervals. In the first case, the $\delta^{37}Cl$ rise will be accompanied with increasing temperature, Cl and Br concentrations, together with decreasing pH and lake volume, following the arrival of new magma or a prominent change in subsurface conditions that enhanced the transport of heat and volatiles such as rock fracturing or rupturing of the solidified shell of an older, cooling intrusion. Alternatively, when the $\delta^{37}Cl$ rise is associated with decreasing temperature, Cl and Br concentrations and increasing pH and lake volume, the internal porosity and permeability is reduced to such an extent that brine input is prevented and volatile supply is restricted to gas input only.

Geochemical modelling has shown that scrubbing of magmatic gas by subsurface water has a strong influence on the rate and composition of fumarolic gas emissions of "wet" volcanoes (Symonds et al., 2001; Marini and Gambardella, 2005). Interaction with a water body will affect primary magmatic gas components to a different extent, depending on their respective solubilities in aqueous systems and on the gas/water ratio. Hence, the presence of water within the edifice of Poás poses limitations to the monitoring of fumarolic gas species with the purpose of detecting the intrusion of magma at an early stage. Instead, our findings indicate that monitoring the $\delta^{37}Cl$ signals as well as Cl and Br contents together with F/Cl and SO_4/Cl ratios in condensates from the CPC fumarole provides information on the status of the subsurface two-phase system, in particular the extent of interaction with liquid water that magma-derived gas experiences en route to the surface. A "dry" pathway is indicated by the combination of low $\delta^{37}Cl$, high temperature, high Cl and Br concentrations, and low F/Cl and SO_4/Cl ratios (Fig. 11). Conversely, high $\delta^{37}Cl$ values, accompanied with low temperatures and Cl and Br concentrations, as well as high F/Cl and SO_4/Cl ratios, point towards extensive interaction with liquid water before the fumarolic gas reaches the surface, indicating a "wet" pathway. The positive correlations between $\delta^{37}Cl$, F/Cl, SO_4/Cl and pH, and inverse correlations with Cl and Br concentrations and temperature (Fig. 11) are consistent with a scrubbing control, in agreement with thermochemical modelling results (Symonds et al., 2001) and the predicted fractionation behaviour of the Cl isotopes (Sharp et al., 2010). Therefore, the time series for the 2.5 years period covered by our data suggests a gradual wetting of the system (Fig. 5). Following these systematics, the opposite sequence (decreasing $\delta^{37}Cl$, SO_4/Cl and F/Cl, increasing temperature, Cl and Br concentrations) would be a signal of system dry-out, which may precede a magmatic eruption. We infer that a predominant influx of brine water during repose intervals produces $\delta^{37}Cl$ and Br/Cl ratios that largely coincide with magmatic values, which can be explained by complete condensation of the deep gases coming from a degassing magma body without any significant phase separation.

The input sources and processes that regulate the shallow lake-hydrothermal system at Poás volcano can be deduced when combining $\delta^{37}Cl$ signatures of Laguna Caliente and CPC fumaroles with S_T/Cl (lake

water) or SO_4/Cl (gas condensates) ratios, taking temperature and status of activity into account (Fig. 12). The primary magmatic source is represented by the composite high-T (>600 °C) Poás gas end-member, having a S_T/Cl ratio defined by an average of CPC high-T gas, and a $\delta^{37}Cl$ value corresponding to the average for condensate samples. Compared to this magmatic gas composition, the CPC high-T condensate has a significantly lower SO_4/Cl ratio due to loss of sulphur, which precipitates when the gas cools down and interacts with water. The low-T (<200 °C) CPC condensates with high $\delta^{37}Cl$ values represent scrubbed gas that already interacted with a shallow water body before reaching the surface. The acid hot spring water of Río Agrio is taken as analogue of brine water from within the volcanic edifice that also feeds the lake. In this simplified scheme, the lake water composition can be created by input from a combination of these end-members. During most of the time covered by our data set, the lake composition was close to brine water, suggesting that this is a dominant input source. Strongest deviations are seen during Stage III and Substage IVC when increased $\delta^{37}Cl$ suggest a prevailing input of ^{37}Cl-enriched gas that had experienced subsurface scrubbing. During the active Stage III, excess gas input is consistent with the occurrence of phreatic eruptions. Evaporation of HCl, driven by the lowered pH and temperature rise due to the large input of volatiles and heat, also contributed to ^{37}Cl-enrichment in the lake water. For the quiet Substage IVC, when the system was cool and conduits were largely clogged, the $\delta^{37}Cl$ increase can be attributed to a reduced supply of brine water, and input being restricted to low-T gas. The samples from Stage V with the highest S_T/Cl ratios point to an input of high-T gas in addition to brine, in agreement with the high activity and frequent occurrence of phreatic eruptions during this period.
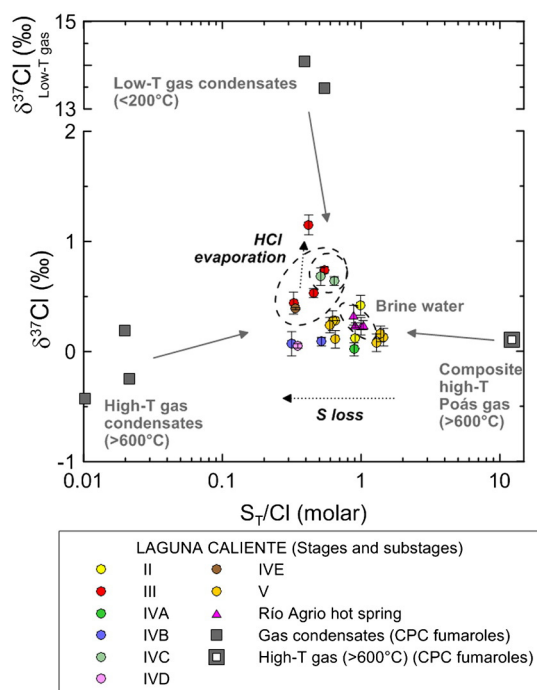
Fig. 12. Input sources and processes responsible for the composition of Laguna Caliente, inferred from relationships between $\delta^{37}Cl$ values and molar S_T/Cl ratios. The lake compositions can be made up via input of (1) brine water, represented by the water from Río Agrio hot spring, (2) high-T magmatic gas, (3) high-T gas condensates and (4) low-T gas condensates, which are all represented by data from the CPC fumaroles. The composite high-T gas (>600 °C) is an average of chemical compositions from OVSICORI (unpublished data) and $\delta^{37}Cl$ values from this study. The gas condensates have experienced loss of sulphur relative to the composite high-T gas, which resulted in lower S_T/Cl ratios (here as measured SO_4/Cl ratios). Note that variations in lake compositions can be explained by shifts in the proportions of the input sources that correspond to the activity sub(stages) defined by Martínez (2008), see text for details. The $\delta^{37}Cl$ error bars in gases and gas condensates do not exceed the size of the symbols.

6. Conclusions

Temporal changes in $\delta^{37}Cl$, Cl–Br concentrations and Br/Cl ratios in the hyperacid water of Laguna Caliente (1985–2012) and subaerial fumaroles (2010–2012) reflect variations in the mode and magnitude of volatile supply. Most of the variations can be attributed to the interaction between magma-derived gas and liquid water in the volcanic–hydrothermal system below the crater.

The $\delta^{37}Cl$ variations in the lake water are moderate (between 0.02 ± 0.06‰ and 1.15 ± 0.09‰) and are associated with changes in the input and output of Cl-bearing fluid phases. The lowest values, which likely approximate magmatic signatures, result from Cl supply through brine influx or high-temperature (>600 °C) subaqueous fumarolic activity. High values correspond to periods either when water temperatures were high (>60 °C) and the budget of dissolved Cl was influenced by $HCl_{(g)}$ evaporation, or when input was probably restricted to low-temperature (<200 °C) gas condensates. A relatively strong Br/Cl diversity is recorded in the lake water. Lowest Br/Cl ratios are presumably close to values of primary gaseous emissions from cooling magma, whereas elevated ratios are either due to preferential input of Br-enriched steam originating from phase separation/boiling at depth, and/or to loss of Cl through evaporation of $HCl_{(g)}$ from the lake surface.

Changes in $\delta^{37}Cl$ and halogen contents of fumarole condensates can be explained as a result of subsurface interaction between deeply derived gas and shallow liquid water. A large range in $\delta^{37}Cl$ (from −0.43 ± 0.09‰ to +14.09 ± 0.08‰) is attributable to partial scavenging and fractionation, with highest values, together with lowest temperatures and Br-Cl concentrations, being generated when the gas/water ratio is low and scavenging is most effective. Our data thus corroborate the earlier result of Sharp et al. (2010) that the absence of an aqueous phase in the system is often expressed by low $\delta^{37}Cl$ in high-temperature fumaroles.

Our findings at Poás volcano demonstrate that combined monitoring of $\delta^{37}Cl$ and Br-Cl signatures of fluids over longer periods of time provides insights into active processes in the vapour–liquid system between intruded magma and the surface as well as into the input–output controls that regulate the behaviour of the lake.

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