The Last Eighteen Years (1998–2014) of Fumarolic Degassing at the Poás Volcano (Costa Rica) and Renewal Activity

Orlando Vaselli, Franco Tassi, Tobias P. Fischer, Daniele Tardani, Erick Fernández, María del Mar Martínez, Marteen J. de Moor and Giulio Bini

Abstract

This chapter reviews the geochemical and isotopic data from the fumarolic gas discharges collected in a discontinuous mode from 1998 to 2014 at Poás volcano. During this period, the "Tico" volcano experienced a renewed phreatic activity that started in 2006 after a couple of decades of relative quiescence. In January 2009, a 6.2 Mw earthquake hit the village of Cinchona, which is located a 4 km to the east of Poás. As the phreatic activity kept evolving, the hyperacidic lake ("Laguna Caliente") dried out and the high-temperature fumaroles that previously were likely entering the lake were revealed, though not accessible. The pyroclastic dome that formed in the early fifties was destroyed at the beginning of 2017 by several relatively small phreatomagmatic (strombolian and vulcanian type) small-size eruptions. The risk of sudden phreatic and phreato-magmatic events prevented the direct sampling of the fumaroles and as a consequence, no geochemical data were sampled in the last three years. Nevertheless, interesting hints were recorded by the gas geochemistry before the 2006 phreatic activity and the 2009 Cinchona seismic events, mainly based on the temporal variations of the H_2S/SO_2, H_2/H_2O, H_2/Ar, CO/CO_2, CH_4/CO_2 and HCl/HF ratios. However, in most cases the geochemical record is not complete since the gas discharging vents migrated or stopped their activity and new fumaroles formed up to the recent visual observations.

Keywords

Poás volcano · Fluid geochemistry · Volcanic hazard · High-temperature fumaroles · Volcanic gases · Phreatic eruptions

1 Introduction

The chemical substances emitted during volcanic eruptions and harsh fumarolic activity play an important role on atmospheric and climatic

O. Vaselli (✉) · F. Tassi · G. Bini
Department of Earth Sciences, Via G. La Pira 4,
50121 Florence, Italy
e-mail: orlando.vaselli@unifi.it

O. Vaselli · F. Tassi
CNR Institute of Geosciences and Earth Resources,
Via G. La Pira 4, 50121 Florence, Italy

T. P. Fischer
Department of Earth and Planetary Sciences,
University of New Mexico, Albuquerque, NM
87131-1116, USA

D. Tardani
Departamento de Geología, Plaza Ercilla 803,
Santiago, Chile

E. Fernández · M. del Mar Martínez · M. J. de Moor
Volcanological and Seismological Observatory,
OVSICORI-UNA, Heredia 2386-3000, Costa Rica

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processes. The released fluids carry useful information about sub-surface processes and it is well established that direct gas monitoring is an important tool for the surveillance of active and quiescent volcanoes (e.g. Chiodini et al. 1995; Giggenbach 1987, 1996; Shinohara et al. 2002, 2015; Vaselli et al. 2010; Fischer et al. 2015). According to Menyalov (1975), variations in terms of "*endogenetic and exogenetic factors*" are expected to be recorded in the chemical and isotopic compositions of the discharging gases, although secondary effects related to reactions with atmospheric gases, underground waters, hosting rocks, redox conditions and bacterial metabolism may complicate the picture recorded at the fumarolic vents (e.g. Symonds et al. 2001).

Volcanic gas monitoring is based on repeated periodic (weekly, monthly, seasonally, annually) sampling of selected fumaroles since the chemical composition of a single fumarole from a volcanic edifice is not representative of the system as a whole. As a routine procedure, fumaroles characterized by different outlet temperatures and located in the surrounding areas, are to be sampled (e.g. Vaselli et al. 2006 and references therein). However, it frequently occurs that although more teams may be working in the same volcanic system, it often happens that the sampling activity is not carried out from the same fumarolic vent(s). This may pose some problems when comparing the geochemical and isotopic data gathered by several teams of volcanologists, since compositional variations of fluids emitted from different gas discharges of a volcanic system are relatively common. To make the general picture more complicated, time migration of fumarolic vents is quite common. This implies that when periodic gas sampling is planned, the selected fumaroles may have disappeared or migrated; thus the newly-born fumaroles may present chemical compositions that can be different with respect to the previously collected sampling sites without any significant variations of the magmatic plumbing system. This is the case at Poás volcano, which has shown a strong compositional variability of the fumarolic gas discharges accompanied by the appearance and disappearance or shifting of fumarolic vents in the last two decades (Vaselli et al. 2003; Fischer et al. 2015).

The present chapter is aimed to summarize and discuss the major chemical and isotopic variations that have characterized the Poás crater fumaroles from 1998 to 2014. In 1998, a bilateral project between the OVSICORI-UNA (Observatorio Vulcanológico y Sismológico de Costa Rica, Universidad Nacional) and the CNR-IGG (National Research Council—Institute of Geosciences and Earth Resources) and the Department of Earth Science (DES) of the University of Florence (Italy) started during which a periodic, though discontinuous, sampling of the Poás crater fumaroles to evaluate the status of the volcano was carried out. This collaboration continued up to 2011 when the last gas sampling was carried out. Additional and important data derived by an NSF project (Resp. TPF) are included in the chapter. Thus, the geochemical and isotopic data related to direct sampling and published by Vaselli et al. (2003), Zimmer et al. (2004), Hilton et al. (2010) and Fischer et al. (2015) were used to depict a comprehensive study on one of the most active volcanoes in Central America by also adding unpublished data produced by the Italian-Costa Rican team. In the last few years, the intense phreatic and phreato-magmatic events (see for further details Martínez et al. Chapter "Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights Into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles"; Mora Amador et al. Chapters "The Extraordinary Sulfur Volcanism of Poás from 1828 to 2018" and "Volcanic Hazard Assessment of Poás (Costa Rica) Based on the 1834, 1910, 1953–1955 and 2017 Historical Eruptions"; Rouwet et al. Chapter "39 Years of Geochemical Monitoring of Laguna Caliente Crater Lake, Poás: Patterns from the Past as Keys for the Future") prevented any direct gas sampling during this time by the Italian-Costa Rican team.

2 A Chronological Summary of the Fumarolic Gas Migration at Poás Volcano in the Last Eighteen Years and the Renewal Activity

The largest historical eruption at Poás volcano occurred in 1910 when a volcanic plume, up to 8 km high, was formed and about 800,000 m^2 of ash covered the volcano summit (namely, the Active Crater) and surrounding areas (e.g. Krushensky and Escalante 1967; Raccichini and Bennett 1977; Vargas 1979; Boza and Mendoza 1981; Lopes 2005; Martínez 2008; Rymer et al. 2010; Mora Amador et al. Chapter "Volcanic Hazard Assessment of Poás (Costa Rica) Based on the 1834, 1910, 1953–1955 and 2017 Historical Eruptions"). In 1953–1955 a short-lived and moderate size eruption formed a $\approx$ 25 m high intra-crater dome (commonly called, pyroclastic dome or pyroclastic cone or simply the dome) and a pit crater into which part of the dome collapsed (e.g. Krushensky and Escalante 1967; Prosser and Carr 1987; Martínez 2008; Mora Amador et al. Chapter "Volcanic Hazard Assessment of Poás (Costa Rica) Based on the 1834, 1910, 1953–1955 and 2017 Historical Eruptions"). Subsequently, a hyperacidic (pH < 1) lake (Laguna Caliente nested in the so-called Active Crater) intermittently appeared and it was relatively stable from 1965 to 1987, though alternated with sporadic geyser activity (e.g. Rymer et al. 2009; Rouwet et al. Chapter "39 Years of Geochemical Monitoring of Laguna Caliente Crater Lake, Poás: Patterns from the Past as Keys for the Future"). Presently, the latest phreatic activity (started in 2006 and still ongoing) dried the lake out and destroyed the 1953–1955 pyroclastic dome (Martínez et al. Chapter "Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights Into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles"; Mora Amador et al. Chapter "Volcanic Hazard Assessment of Poás (Costa Rica) Based on the 1834, 1910, 1953–1955 and 2017 Historical Eruptions"; Rouwet et al. Chapter "39 Years of Geochemical Monitoring of Laguna Caliente Crater Lake, Poás: Patterns from the Past as Keys for the Future").

Explosions characterized by the emissions of sulfur-encrusted blocks (Bennett and Raccichini 1978; Bennett 1979; Francis et al. 1980) in 1978 and the presence of volcanic liquid sulfur (e.g. Oppenheimer and Stevenson 1989; Oppenheimer 1992; Mora Amador et al. Chapter "The Extraordinary Sulfur Volcanism of Poás from 1828 to 2018") was revealed at Laguna Caliente when in 1981 the outlet temperatures of the fumaroles were up to 1020 °C, suggesting that a new cycle of activity had commenced (Casertano et al. 1987; Rymer et al. 2000, 2009; Martínez et al. 2000; Martínez 2008). In 1989 the lake dried out and the crater bottom was visible (e.g. Rymer et al. 2009; Martínez et al. Chapter "Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights Into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles") (Fig. 1). After a sequence of phreatic eruptions (Fig. 2), the Laguna Caliente once again disappeared in 1990, 1991, 1992, 1993 and 1994 (Martínez et al. 2000, Chapter "Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights Into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles"; Martínez 2008). The acidic crater lake restored in mid-1995, although significant variations in terms of lake level and chemistry were observed (e.g. Rowe et al. 1992, 1995; Rowe 1994; Martínez et al. 2000; Rouwet et al. Chapter "39 Years of Geochemical Monitoring of Laguna Caliente Crater Lake, Poás: Patterns from the Past as Keys for the Future" and references therein).

The below reported observations provide details on the presence and migration of the fumarolic gas discharges and are part of the observations that the OVSICORI personnel provided in their bulletins (http://www.ovsicori.una.

Fig. 1 The crater bottom after the Laguna Caliente dried out in 1989

Fig. 2 A small phreatic eruption at Poás volcano in 1989

ac.cr/) and forwarded to the Global Volcanism Program of the Smithsonian Institute (http://volcano.si.edu/) as well as from Martínez (2008). During the period considered in this chapter, the fumarolic activity was mainly located close to the pyroclastic dome while other areas from the inner flanks of the Active Crater were affected by the presence of new fumaroles, whose activity waned with time until they disappeared and occasionally new fumaroles formed. It is noteworthy to mention that the outlet temperatures recorded after November 2008 at the interface between the Laguna Caliente and the pyroclastic dome have to be considered with caution since the fumarolic gas discharges were quite difficult to be reached and measured.

In 1998, when the periodic geochemical survey was carried out in the framework of the collaboration between OVSICORI and CNR-IGG and DES, gas bubbling was noticed around the pyroclastic dome and along the lower part of the eastern inner terrace of the Active Crater. It is to mention that vigorous discharge around the pyroclastic dome started in September 1995 accompanied by small flows of bright molten sulfur (temperature was around 113–119 °C) and strong sulfur smell, after a 7-years period of only fairly weak fumarolic activity around the pyroclastic dome. The Laguna Caliente volume increased in a steady fashion throughout 1995–1997, reaching a record level between September and December 1997, partly due to above-average rainfall. A small hydrothermal explosion occurred in the northern side of the dome on April 1996, turning the lake color from milky turquoise to grey for several weeks (Martínez et al. Chapter "Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights Into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles"). Interestingly, polythionates reappeared abruptly in the acidic lake in February 1996 with a 3-fold to 6-fold increase in the $S_4O_6^{2-}/S_5O_6^{2-}$ and $S_4O_6^{2-}/S_6O_6^{2-}$ ratios, respectively, after being practically absent during most the 1987–1995 period. This suggested and input of fresh S-rich magmatic gases into the Laguna Caliente. In addition, in ca. 40 year of geochemical observations at Laguna Caliente, between late 1996 and mid-2004, the lake brines unusually enriched in chloride with respect to sulfate (Martínez 2008; Martínez et al. Chapter "Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights Into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles"). From 1999 to 2000, fumarolic gas vents were observed around the pyroclastic dome and along the lower part of the eastern terrace at the active crater (e.g. Fumarole Norte). In March 1999, several acidic springs discharged waters along the lower part of the inner eastern terrace. On September 28, 1999, a fumarolic plume (about 2 km high) formed above the pyroclastic dome. Between December 1999 and February 2000, seismic signals corresponding to tremor increased. In February 2000, 24 h of tremor were recorded on a single day, 11 h of which corresponded to monochromatic tremor. From March 2001 to September 2001, new fumarolic vents opened in the eastern area of the inner crater and a relatively strong degassing was observed through the pyroclastic dome. Enhanced fumarolic degassing was accompanied by increasing seismic activity. For instance, in March 2001, 35 h of polychromatic tremor were recorded in a matter of 3 consecutive days. In 2000 and 2001, fumaroles and springs along the eastern terrace registered temperature of 88–95 °C and 66-89 °C, respectively. From October 2001 to February 2005, the fumarolic outgassing through the pyroclastic dome remained relatively weak and practically unnoticeable between late 2003 and throughout 2005. Similar to the fumarolic activity occurring close to the pyroclastic dome, Laguna Caliente remained relatively quiet during this time period except for some upwelling, floating molten sulfur and persistent emanation of fumes, particularly from August 2002 to December 2003.

The fumarolic activity in the eastern part of the crater maintained relatively vigorous. At the Fumarole Norte, outlet temperatures >110 °C were recorded in March 2003. Between late 2003 and early 2005, the lake volume dramatically increased, reaching its highest level since the late seventies, provoking a water overflow in the eastern edge of the lake and submerging some sub-aerial fumaroles for several weeks in early 2005.

In March 2005, a new period of strong convective activity and evaporation at Laguna Caliente commenced after 11 years of relative quiescence, changing drastically the color and chemistry of the lake, suggesting an increase in the input of heat and volatiles through the subaqueous fumarolic discharges. Simultaneously, Fumarole Norte showed a significant increase in temperature (from 105 °C in March 2005 to 203 °C in May-June 2005). Unusually high seismic activity paralleled these drastic changes, especially in 2005. Between March 2005 and early 2006 the lake level dropped by 10 m. The fumarolic activity around the pyroclastic dome showed a gradual increase in the degassing rate from April 2005 onwards although the temperature remained around 92 °C. From March 2006, the phreatic activity resumed in the Laguna Caliente after 12 years of relative quiescence. The renewal of phreatic activity was preceded and accompanied by an abrupt increase of both the seismic activity and most outlet temperatures of the fumarolic discharges. Phreatic explosions were observed in March, April, September and December 2006. No phreatic explosions were recorded in 2007, although strong degassing and convection were observed in the Laguna Caliente, producing a significant lowering of the water level and an increase of the water temperature (up to 60 °C). Springs and fumaroles that appeared in the eastern terrace in early 1999–2000 dried out or disappeared in 2007. In October 2007, fumarole temperatures at the pyroclastic cone reached 101 °C. In 2008, new phreatic eruptions occurred, generating muddy water columns reaching to ca. 200 m above the lake surface and leaving fragments of altered rocks and molten sulfur dispersed on the crater floor. In November 2008, the temperatures of the fumaroles close to the pyroclastic dome were 322 °C, although in early December 2008 they apparently went down to 95 °C. A decrease of the water temperature (45 °C in November 2008 to January 2009) of the Laguna Caliente was also recorded. On the 7th and 8th of January 2009, two shallow earthquakes (6.5–7.0 km deep) hit the surroundings of Poás volcano. The 7th of January 2009 4.5 M earthquake occurred at 10:00 a.m. local time 4 km N-NE of Fraijanes Sabanilla of Alajuela, while on the 8th of January 2009 a 6.2 M earthquake (estimated depth: 6.0 km) occurred at 13:21 local time, just 1 km south of Cinchona of Poás Alajuela (e.g. Barquero 2009; Alvarado 2010; Fernández-Arce and Mora Amadora, Chapter "Seismicity of Poás Volcano, Costa Rica"; Ruiz et al. Chapter "Geochemical and Geochronological Characterisation of the Poas Stratovolcano Stratigraphy"). Between January and July 2009 soon after these quakes hit the region, the lake showed a strong release of highly corrosive gases at its surface and large convective cells formed. A rapid uprising in acidity and concentration of dissolved volatiles and rock-forming elements occurred. The temperature fluctuated around 45–51 °C. Between January and March 2009 small phreatic eruptions were recorded. In May 2009, the pH of the lake was very low ($pH = -0.72$). The pH, temperature, and electrical conductivity of Laguna Caliente approached the values measured in the period 1986–1989 when the lake level was reduced and dried out completely in April 1989. Although between 2005 and 2015 the lake was affected by strong fluctuations in volume, the water levels did not reach those recorded between 1986 and 1994. The pyroclastic dome fumaroles remained around 93 °C, although in June 2009 the outlet temperature at some accessible sites around the pyroclastic dome was of 123 °C. In September 2009 the lake level dropped by about 4 m relative to that recorded in August 2009 and the temperature increased up to 55 °C. Between September and December 2009 the outlet temperatures of the pyroclastic dome fumaroles increased (to 150 and 665 °C). On the 24th and 25th of December two phreatic eruptions occurred, the later producing a phreatic plume of ca. 600 m above the surface of the lake. In January to February 2010, small to medium phreatic eruptions were reported by the park rangers. On the 23rd of February, a phreatic eruption produced a water and steam column of ca. 1 km above the lake surface. The outlet temperatures of the fumaroles around the pyroclastic dome was approaching 640 °C. Between March and May 2010, two small phreatic eruptions were observed by the park rangers and the fumaroles at the pyroclastic dome were up to 838 °C. Between June and December 2010, small to medium size phreatic eruptions were recorded (Fig. 3) and water and fumarole temperature reached to 64 and 865 °C, respectively. From January to April 2011, the fumarolic discharges close to the pyroclastic dome reached 600 °C and gas bursts and small phreatic explosions were noticed in the central part of the lake. In June 2011 the dome fumaroles reached a temperature of 663 °C and several small to moderate size phreatic eruptions (more than 100 events of a few dozens of meters of height) were registered. From July to September 2011, the dome fumaroles showed temperatures up to 890 °C (Fig. 4) and incandescence was observed even under day light conditions. Small phreatic eruptions continued to occur from July to August 2011. From October to December 2011 and in February 2012, the outlet temperature of the dome fumaroles dropped to 730 °C and no phreatic activity was observed. In March-June 2012, the dome fumaroles further dropped in temperature to 610 °C and a 500 m high phreatic eruption occurred on the 15th of May. In July 2012, the dome fumaroles showed a sharp decrease (down to 302 °C), accompanied by several small phreatic explosions occurred, the most important being the one on the 30th of July. In August to September 2012, the dome fumaroles showed temperature <200 °C and no phreatic eruptions were observed, whereas in October 2012 at least ten small to moderate size phreatic explosions were recorded. On the 20th of October 2012, about 95% of the lake surface was covered by slicks of molten sulfur. In November 2012, the temperatures at the dome fumaroles were clustering around 170 °C and small phreatic explosions occurred in the lake. The phreatic activity continued up to August 2013. In April 2013, the dome fumaroles reached a temperature of 380 °C and increased to 600 °C in August 2013. Then, at the end of 2013, the temperature was of about 400 °C whilst from January to April 2014, it was fluctuating between 600 and 720 °C. A number of phreatic eruptions occurred between February and June 2014. The lake water temperature was relatively stable, ranging between 45 and 55 °C. Between July and September 2014, the dome fumaroles showed no significant variations in terms of outlet temperatures and numerous phreatic explosions were recorded, most of them being of small size (30–50 m high), with the exception of those occurring on the 31st of July and the 27th of August, when up to 200 m high plumes were recorded. In April 2013 and July and September 2014, the flux rate of SO_2 was measured by mobile DOAS with values of 120, 530 and 240 ton/day, respectively (e.g. Martínez et al. Chapter "Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights Into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles" and references therein).

From October 2014 to August 2015, the phreatic activity at Poás volcano ceased. In May 2015 the fumaroles on the pyroclastic cone temperature had a temperature of 625 °C while in August 2015 it was 360 °C. In October 2014, two important phreatic episodes occurred (250 m high) a few days after the strong emission of flashes of hot gases through the pyroclastic dome. In August 2015 the lake had a temperature of only 31 °C with its water level rapidly rising up since late 2014.

In summary, the cycle of phreatic activity that started in 2006 and continued almost uninterruptedly until October 2014 coincided with a significant increase of the temperatures at the dome fumaroles. Furthermore, it has to be mentioned that over the last 40 years, Poás has experienced 3 stages of phreatic activity that were alternated with periods of quiescence in cycles of 6 to 10 years. In April 2017 a new phase opened, when phreatic and phreatomagmatic events occurred, the latter of which destroyed the 1953–1955 dome (Martínez et al. Chapter "Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights Into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles"; Mora Amador et al. Chapter "Volcanic Hazard Assessment of Poás (Costa Rica) Based on the 1834, 1910, 1953–1955 and 2017 Historical Eruptions"; Rouwet al. Chapter "39 Years of Geochemical Monitoring of Laguna Caliente Crater Lake, Poás: Patterns from the Past as Keys for the Future"). From the second

Fig. 3 A small phreatic eruption inside the Laguna Caliente taken on the 14th of August 2010

Fig. 4 Aerial photo of the fumarolic vents at the interface between the Laguna Caliente and the pyroclastic dome. The right-hand side fumarole shows a typical bluish color, indicative of the presence of SO_2 and fine sulfate-rich aerosols

half of 2017 to early 2018, the volcanic activity ceased and low temperature fumaroles and sporadic mud-pools at the dried bottom of the Active Crater remained (Martínez et al. Chapter "Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights Into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles").

3 Sampling Sites and Analytical Methods

Owing to the different status of the volcanic system from 1998 to 2014 as well as the appearance and disappearance of new fumarolic vents, there is no continuous record for most of the studied fumaroles with the exception of the pyroclastic dome fumaroles (“Dome” hereafter), although there is a gap of sampling between 2000 and 2007. Relatively long-term chemical compositions are available for the **Fumarole Norte** (namely the “Naranja” fumarole in Hilton et al. 2010 and Fischer et al. 2015), **La Niña** and **Fumarole Este** (namely, the “Official” in Hilton et al. 2010 and Fischer et al. 2015). Sporadic samplings were thus performed at the fumaroles **Pared Sur**, **Fumarole SE**, **Fumarole NE**, **Fumarole BP** (boiling pool) and **Fumarole ENE**. One gas sample was collected inside the Laguna Caliente (**Lake gas**) when a vertical profile of the crater lake was carried out (Vaselli et al. 2003). It is worth to mention that Zimmer et al. (2004), Hilton et al. (2010) and Fischer et al. (2015) have only reported the chemical and isotopic analyses of the Dome, Fumarole Norte and Fumarole Este. Moreover, with the exception of the fumaroles reported in the previously mentioned papers and those described and discussed in Vaselli et al. (2003), all the other data are unpublished. To the best of our knowledge, no gas data are available after 2015.

For the sake of clarity, the location of the fumaroles investigated is reported in Fig. 5a, b along with a detail of the Fumarole Norte (Fig. 5c) and glowing of the Dome fumarole (July 2011; Fig. 5d) with a temperature of 890 °C, the latter being sampled when the outlet

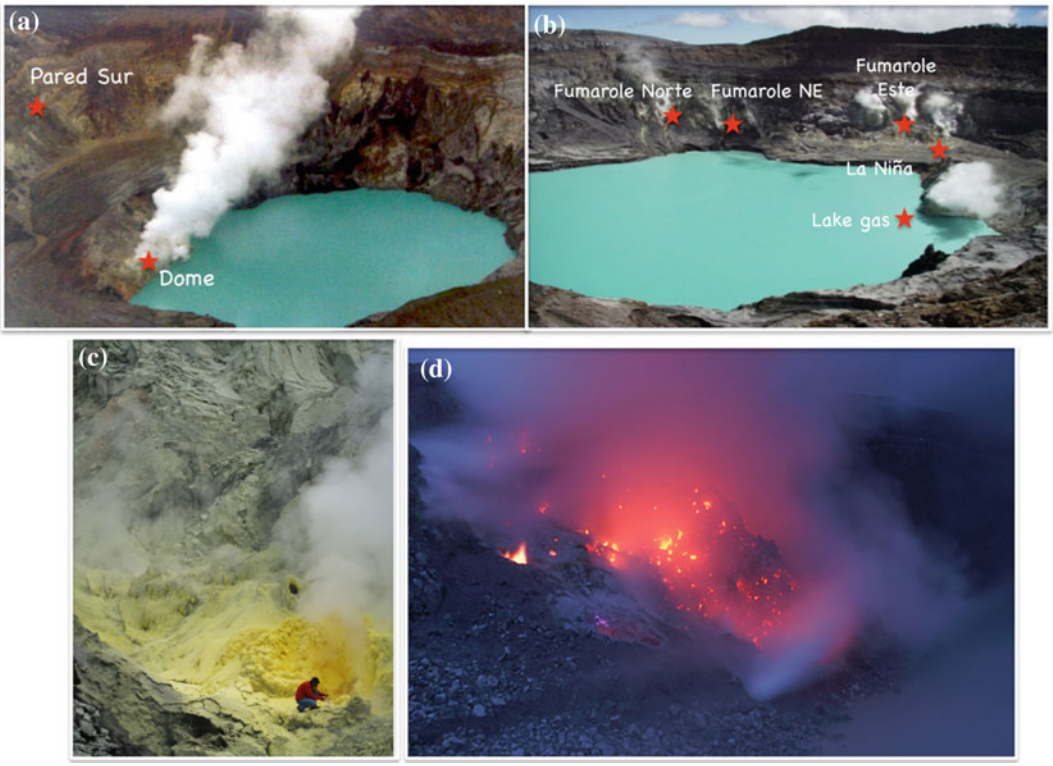

Fig. 5 Sampling location of the Poás fumaroles reported in the present chapter: **a** the Pared Sur and the Dome fumaroles (photo taken in September 1999); **b** the Fumarole Norte, Fumarole NE, Fumarole ENE, Fumarole Este, Fumarole SE, La Niña and the Lake gas (photo taken in February 2004); **c** the Fumarole Norte in March 2007 and **d** the Dome fumarole in July 2011 when the outlet temperature was of 890 °C

temperature was of 375 °C (April 2014, Fischer et al. 2015).

Gas samples for chemical and isotopic composition reported in Zimmer et al. (2004), Hilton et al. (2010) and Fischer et al. (2015) were collected by following the sampling techniques and measured by using the analytical procedures described in Giggenbach and Goguel (1989), Hilton et al. (2002), Zimmer (2002), Mitchell et al. (2010) whereas the methodologies used in Vaselli et al. (2003) and for the unpublished data were reported in Montegrossi et al. (2001) and Vaselli et al. (2006).

4 Results

The chemical (in mmol/mol) and isotopic (helium and argon, carbon in CO_2) composition of the Poás fumarolic discharges produced by the Italian-Costa Rica team (hereafter ICT), also including those from Vaselli et al. (2003), are reported while those produced by the American team (hereafter AT) can be found in Zimmer et al. (2004), Hilton et al. (2010) and Fischer et al. (2015). Most the outlet temperatures of the fumaroles were below 120 °C up to early 2005. Then, 250 °C were recorded in March 2014 (Fumarole Norte, AT). An abrupt increase was then observed at the Dome fumarole (hereafter Dome), whose outlet temperature steadily incremented since September 2009 (480 °C, ICT) and reached 763 °C in June 2010 (ICT). As previously mentioned, after the phreatic events occurring after March 2006, there were some problems in approaching the Dome due to the intense emissions and high temperatures.

All the fumaroles were dominated by steam, whose concentrations were between 725 and 998 mmol/mol with the exception of the gas collected at the surface of the acidic lake (Lake gas in Table 1), which contained the highest H_2 concentrations (February 2001, 31.58 mmol/mol; ICT) recorded at Poás from 1998 to 2014, along with the Dome gases collected in January 2009 by ICT, and that of the Fumarole NE (February 2001; ICT) when it was collected for the first time. CO_2 contents were very variable as they were ranging from 1 to 668 mmol/mol, the highest value recorded in the Lake gas. Lower concentrations were measured for SO_2 (from 0.002 to 247 mmol/mol) and H_2S (from 0.02 and 9 mmol/mol) and, when available, the H_2S/SO_2 was between 0.003 (Fumarole Este, March 2005; AT) and 822 (Pared Sur, February 1999; ICT). H_2S and SO_2 were below the detection limit in the Lake gas. ICT also measured the concentrations of elemental gaseous sulfur (Table 1), with concentrations between 9×10^{-4} and 5.8×10^{-2} mmol/mol.

HCl and HF, with subordinate contents with respect to those of other acidic gases, were varying from 0.0031 and 26 mmol/mol and 0.00001 and 4 mmol/mol, respectively. It is noteworthy to point out that, on average, the highest concentrations of the acidic gases were recorded at the Dome, although CO_2 (245 mmol/mol; ICT), SO_2 (247 mmol/mol; ICT) and H_2S (6.44 mmol/mol; ICT) showed the highest concentrations at the Fumarole ESTE when it was sampled for the first time in February 2001. The N_2/Ar ratios were spanning quite widely, being varying from 44 (suggesting the presence of an atmospheric component) to 13,715 (likely related to a contribution of thermometamorphic component), with the highest values registered at the Dome, with a clear increase with time. Setting aside the previously mentioned gas samples, the H_2 concentrations were comprised between 0.0004 and 11.8 mmol/mol. Consistently with the high concentrations of the acidic gases, the Dome also showed the highest values of H_2, which tended to increase with time. Carbon monoxide showed a behavior similar to that of H_2 and the acidic gases as the highest contents were recorded at the Dome (up to 0.999 mmol/mol). Neon and helium had contents between 4.4×10^{-8} and 5.0×10^{-5} mmol/mol and 4.0×10^{-5} and 7.96×10^{-1} mmol/mol respectively, while the He/Ne ratios were up to 1,900 and constantly higher than 10, with the exception of the Dome (February 2000; ICT).

The helium isotopic ratios (expressed as R/Ra, where R is the measured $^3He/^4He$ in the sample and Ra is the $^3He/^4He$ in the air. The values, corrected for air contamination using the He/Ne

Table 1 Temperature (in °C) and chemical (in mmol/mol) and isotopic ($\delta^{13}C$–CO_2, $^3He/^4He$ expressed as R/Ra corrected for the He/Ne ratio and $^{40}Ar/^{36}Ar$) composition of the fumarolic discharges collected by the Italian-Costa Rican Team

Poas (mmol/mol)	T (° C)	H_2O	CO_2	SO_2	H_2S	S	HCl	HF	N_2	CH_4	Ar	O_2	Ne	H_2	He	CO	$\delta^{13}C$	R/34 Ra	$^{40}Ar/^{36}Ar$
Pared Sur Feb. 1998	93	987	9.90		0.84		0.432		1.198	0.002274	0.01141	0.00001426	0.0000225	0.2793	0.00171	0.00002	n.d.		
Parete Sur Feb. 1999	89	978	18.41	0.002	1.88	0.0001			1.345	0.001163	0.00736	0.00000199	0.0000060	0.0941	0.00226	0.00044	−6.56		
Dome Feb. 1999	95	936	30.07	29.35		0.0034	1.733	0.0040	1.956	0.000226	0.00792		0.0000070	0.4542	0.00149	0.03891	n.d.		
Dome Nov. 1999	95	946	24.11	26.35	0.57	0.0372	1.563	0.0055	1.583	0.000106	0.03267			0.0518	0.00446	0.00953	n.d.	6.65	
Domo Feb. 2000	94	992	0.74	2.95	0.86	0.0165	1.430	0.0068	0.469	0.000075	0.00680		0.0000028	1.9129	0.00002	0.00495	−6.13		
Dome Oct. 2007	90	930	40.02	29.16	0.31	0.0005	0.692	0.0673	0.013	0.000021	0.00010	0.00000185	0.0000001	0.1731	0.00001	0.00050			
Dome Jan. 2008	96	926	46.55	26.45	0.41	0.0004	0.641	0.0515	0.054	0.000026	0.00021	0.00000055	0.0000001	0.1556	0.00002	0.00115			
Dome March 2008	97	912	50.32	36.34	0.35	0.0004	0.501	0.0575	0.066	0.000025	0.00032	0.00000018	0.0000002	0.2084	0.00002	0.00091			
Dome May 2008	109	891	63.37	43.57	0.53	0.0005	1.073	0.1807	0.071	0.000060	0.00008	0.00000123	0.0000000	0.1485	0.00008	0.00061			
Dome June 2008	112	891	61.46	44.85	0.51	0.0003	0.988	0.1544	0.327	0.000048	0.00025	0.00000099	0.0000001	0.2568	0.00005	0.00562			
Dome July 2008	180	872	73.46	51.42	0.56	0.0014	1.215	0.1612	0.715	0.000031	0.00069	0.00000112	0.0000003	0.4551	0.00009	0.02145			
Dome Oct. 2008	276	840	94.58	60.45	0.49	0.0014	1.744	0.1698	0.710	0.000026	0.00060	0.00000068	0.0000003	1.5410	0.00006	0.05845			
Dome Jan. 2009	322	897	61.26	31.65	3.54	0.0041	2.874	0.2045	0.898	0.000015	0.00062	0.00000024	0.0000001	2.9840	0.00009	0.10890			
Dome March 2009	93	952	26.58	15.49	3.08	0.0022	1.105	0.0215	0.665	0.000125	0.00122	0.00000046	0.0000003	0.9842	0.00022	0.02145			
Dome May 2009	93	944	33.27	16.87	3.27	0.0016	0.987	0.0256	0.649	0.000085	0.00099	0.00000039	0.0000002	1.1250	0.00016	0.02645			
Dome June 2009	123	906	61.59	25.65	2.78	0.0018	1.254	0.0985	0.771	0.000036	0.00072	0.00000026	0.0000002	1.8450	0.00011	0.07745			
Dome Aug. 11, 2009	97	931	36.13	27.49	2.56	0.0012	0.845	0.0561	0.649	0.000025	0.00051	0.00000045	0.0000003	1.3540	0.00004	0.04856			
Dome Aug. 31, 2009	116	879	61.55	54.95	0.85	0.0026	1.145	0.0815	0.595	0.000015	0.00047	0.00000070	0.0000003	1.9540	0.00006	0.07941			
Dome Sept. 2009	480	814	104.52	71.46	0.29	0.0051	2.516	0.2154	0.815	0.000005	0.00061	0.00000035	0.0000003	5.2150	0.00008	0.58790			
Dome Oct. 2009	415	822	98.75	70.46	0.42	0.0032	2.611	0.2616	0.755	0.000006	0.00056	0.00000016	0.0000002	4.7150	0.00008	0.48750			
Dome Nov. 2009	665	738	169.47	76.95	0.32	0.0042	4.155	1.6480	0.789	0.000005	0.00063	0.00000038	0.0000003	7.9540	0.00009	0.71520			
Dome Jan. 2010	650	754	156.95	72.15	0.35	0.0085	4.518	1.9450	0.812	0.000005	0.00051	0.00000030	0.0000003	8.1450	0.00007	0.89410			
Dome Mar. 2010	160	796	115.65	68.46	0.69	0.0070	5.071	2.6540	0.718	0.000006	0.00046	0.00000014	0.0000002	9.5610	0.00006	0.91560			

(continued)

Table 1 (continued)

Poas (mmol/mol)	T (°C)	H_2O	CO_2	SO_2	H_2S	S	HCl	HF	N_2	CH_4	Ar	O_2	Ne	H_2	He	CO	$\delta^{13}C$	R/34 Ra	$^{40}Ar/^{36}Ar$
Dome Mar. 2010*	480	765	138.47	75.84	0.38	0.0068	5.584	3.7410	0.670	0.000003	0.00038	0.00000013	0.0000002	9.7450	0.00004	0.88870			
Dome Apr. 2010	566	732	168.41	75.85	0.57	0.0015	6.415	3.1540	0.846	0.000002	0.00019	0.00000006	0.0000001	11.8740	0.00004	0.91480			
Dome May 2010	148	837	94.59	54.87	1.15	0.0008	2.654	0.8542	0.715	0.000002	0.00018	0.00000005	0.0000001	7.4580	0.00005	0.47850			
Dome June 2010	763	725	158.50	91.75	0.85	0.0007	7.841	3.5450	0.618	0.000001	0.00007	0.00000004	0.0000001	10.8450	0.00004	0.99860			
Dome Aug. 2010	650	741	148.46	87.65	1.41	0.0006	7.154	2.9840	0.598	0.000001	0.00007	0.00000002	0.0000001	9.4210	0.00003	0.87550			
Dome Mar. 2011	250	746	158.48	75.99	1.18	0.0004	6.485	2.1140	0.716	0.000002	0.00006	0.00000002	0.0000001	8.4570	0.00003	0.74580			
Dome Apr. 2011	250	759	146.99	76.45	1.25	0.0005	6.187	1.9850	0.698	0.000003	0.00006	0.00000003	0.0000001	6.8570	0.00004	0.69860			
Dome May 2011	280	753	149.85	77.15	1.07	0.0006	6.845	2.2180	0.658	0.000002	0.00005	0.00000002	0.0000001	8.1150	0.00003	0.81140			
Fumarole Este Feb. 2001	97	923	74.22	1.14	0.26	0.0141	0.473		0.573	0.000001	0.00627	0.00013586	0.0000036	0.0005	0.00005		−4.29		
Fumarole Este Feb. 2004	99	967	22.81	8.54	0.79	0.0006	0.751	0.0001	0.054	0.000001	0.00043	0.00000188	0.0000003	0.0012	0.00002	0.00002			
Lake gas Feb. 2001	78	282	668.00						15.899	0.000312	0.05547	0.00141086	0.0000320	31.5855	0.00001	0.02199	n.d.		
Fumarole NE Feb. 2001	101	498	245.57	247.04	6.44	0.0576	2.294	0.0002	0.758	0.000026	0.01058		0.0000063	0.0252	0.00089	0.00041	n.d.		
Fumarole NE Aug. 2001	101	794	82.12	118.22	4.30	0.0031	0.665	0.0000	0.446	0.000002	0.00767		0.0000036	0.0265	0.00030	0.00105	n.d.		
Fumarole NE Nov. 2001	104	852	117.61	29.05	0.68	0.0015	0.172	0.0001	0.959	0.000003	0.00458	0.00000921	0.0000019	0.0049	0.00025	0.00250	n.d.		
Fumarole NE Feb. 2002	103	931	34.52	26.38	0.16	0.0017	7.937	0.0366	0.076	0.000000	0.00023	0.00000010	0.0000001	0.0061	0.00006	0.00007	n.d.		
Fumarole NE Apr. 2002	98	799	140.64	57.77	1.08	0.0018	0.554	0.0022	1.083	0.000121	0.00597	0.00013264	0.0000042	0.0059	0.00020	0.00044	n.d.		
Fumarole NE Apr. 2003	118	921	40.95	35.95	1.18	0.0006	0.911	0.0006	0.085	0.000184	0.00189	0.00000368	0.0000016	0.1032	0.00003	0.00003	n.d.		
Fumarole NE Jul. 1, 2003	116	948	26.35	23.12	0.18	0.0007	1.394	0.0001	0.776	0.000004	0.00268	0.00000761	0.0000016	0.0318	0.00015	0.00094			
Fumarole NE Jul. 29, 2003	116	941	29.21	27.65	0.34	0.0003	1.899	0.0001	0.241	0.000002	0.00089	0.00000215	0.0000005	0.0067	0.00004	0.00025			
Fumarole NE Apr. 2004	115	944	26.40	21.47	0.18	0.0007	1.561	0.0001	5.976	0.000302	0.02117	0.00001473	0.0000118	0.5631	0.00016	0.00740	−3.06	7.47	325

(continued)

Table 1 (continued)

Poas (mmol/mol)	T (° C)	H_2O	CO_2	SO_2	H_2S	S	HCl	HF	N_2	CH_4	Ar	O_2	Ne	H_2	He	CO	$\delta^{13}C$	R/34 Ra	$^{40}Ar/^{36}Ar$
Fumarole NE Jun. 2007	116	907	44.99	43.82	0.47	0.0003	0.444	0.0011	0.142	0.001110	0.00079	0.00002527	0.0000005	3.0024	0.00031	0.00027			
Fumarole NE Sep. 2007	113	901	48.75	46.28	0.48	0.0004	0.550	0.0045	0.251	0.001218	0.00099	0.00002097	0.0000005	2.9326	0.00023	0.00030			
La Niña Feb. 2001	95	929	64.70		5.39	0.0029			0.409	0.000004	0.00419	0.00000663	0.0000028	0.0005	0.00015	0.00005	−2.57		
La Niña Nov. 2001	81	970	28.88		1.25	0.0006	0.003	0.0000	0.129	0.000003	0.00062	0.00000669	0.0000003	0.0084	0.00029	0.00003	−3.54		
La Niña Feb. 2002	86	963	36.22		0.60	0.0005	0.018	0.0001	0.124	0.000003	0.00042	0.00000024	0.0000003	0.0103	0.00024	0.00008	n.d.		
La Niña Apr. 2002	93	962	36.25	0.25	1.08	0.0010	0.082	0.0240	0.050	0.000001	0.00016	0.00000002	0.0000001	0.0041	0.00014	0.00001	−3.12		
La Niña Apr. 2, 2003	97	931	42.94	24.32	0.36	0.0009	1.576	0.0001	0.149	0.000024	0.00335	0.00001049	0.0000030	0.0004	0.00005	0.00009	n.d.		
La Niña 28 Apr., 2003	97	908	56.91	33.87	0.49	0.0007	0.300	0.0000	0.173	0.000123	0.00306	0.00000385	0.0000028	0.0008	0.00010	0.00017	n.d.		
La Niña Apr. 2004	94	963	31.01	0.26	0.35	0.0005	0.240	0.0000	4.622	0.000020	0.00994	0.00007624	0.0000065	0.3113	0.00014	0.00307	n.d.		
La Niña Feb. 2005	94	959	30.61	10.39	0.12	0.0006	0.038	0.0000	0.103	0.000001	0.00104	0.00000003	0.0000006	0.0132	0.00015	0.00006	n.d.		
La Niña Apr. 2005	94	984	13.29	1.97	0.38	0.0004	0.242	0.0000	0.024	0.000004	0.00053	0.00000003	0.0000003	0.0096	0.00006	0.00002	n.d.		
Fumarole Norte Feb. 2001	95	976	15.86	6.82	0.22	0.0011	0.274	0.0001	1.122	0.000016	0.00459			0.1691	0.00153	0.00097	n.d.		
Fumarole Norte Nov. 2001	101	895	63.32	40.63	0.74	0.0030	0.420	0.0002	0.197	0.000003	0.00100	0.00000019	0.0000004	0.0209	0.00066	0.00021	−2.90		
Fumarole Norte Nov. 2001	101	929	32.01	34.22	0.76	0.0016	3.490	0.0280	0.103	0.000001	0.00059	0.00000303	0.0000002	0.0085	0.00008	0.00005	−3.70		
Fumarole Norte Jan. 2002	101	929	37.33	28.98	1.03	0.0007	3.357	0.0270	0.089	0.000001	0.00042	0.00000006	0.0000002	0.0068	0.00015	0.00003	n.d.		
Fumarole Norte Feb. 2002	101	952	28.70	17.05	0.65	0.0010	1.926	0.0155	0.119	0.000001	0.00060	0.00000938	0.0000002	0.0054	0.00010	0.00032	n.d.		
Fumarole Norte Apr. 2002	94	901	62.75	31.60	0.56	0.0030	0.488	0.0124	3.001	0.000005	0.01685	0.00015727	0.0000117	0.0107	0.00030	0.00173	n.d.		
Fumarole Norte May 2002	99	943	49.12	4.25	1.33	0.0006	1.406	0.4508	0.256	0.000001	0.00132	0.00000104	0.0000011	0.0043	0.00010	0.00006	−2.90		
Fumarole Norte Jul. 2002	88	908	53.14	36.23	0.66	0.0017	1.307	0.4204	0.207	0.000001	0.00105	0.00000330	0.0000009	0.0077	0.00005	0.00025	n.d.		

(continued)

Table 1 (continued)

Poas (mmol/mol)	T (°C)	H_2O	CO_2	SO_2	H_2S	S	HCl	HF	N_2	CH_4	Ar	O_2	Ne	H_2	He	CO	$\delta^{13}C$	R/34 Ra	$^{40}Ar/^{36}Ar$
Fumarole Norte Apr. 2003	93	947	34.73	17.09	0.75	0.0008	0.120	0.0462	0.088	0.000005	0.00046	0.00000149	0.0000004	0.0035	0.00002	0.00030	−2.71		
Fumarole Norte Apr. 2004	97	928	36.00	12.37	0.87	0.0025	2.369	0.0003	19.333	0.000101	0.09864	0.00010087	0.0000547	0.7227	0.00071	0.01914	n.d.		
Fumarole Norte Aug. 2004	95	936	23.17	39.76	0.74	0.0004	0.245	0.0008	0.092	0.000001	0.00060	0.00000172	0.0000004	0.0040	0.00008	0.00009	n.d.		

ratios, were in a relatively narrow range, from 6.64 (Fumarole ESTE, November 2006; AT) to 7.47 (Fumarole NE, April 2004; ICT). The carbon isotopes in CO_2 (expressed as $\delta^{13}C–CO_2$ ‰ vs. V-PDB) showed a higher variability as they were ranging from −6.8 (Fumarole Este, March 2001 AT) to −1.3 (Eastern Flank June 2005 AT) ‰ versus V-PDB. Few samples were analyzed by AT for nitrogen isotopes in N_2 (expressed as $\delta^{15}N–N_2$ ‰ vs. NBS-AIR) with values from −3.0 (Fumarole ESTE July 2001; AT) to 1.9 (Fumarole ESTE March 2003; AT) ‰ versus NBS-AIR. The chlorine isotopes (expressed as $\delta^{37}Cl$‰ vs. SMOC), measured in the Este and Norte fumaroles (AT) varied between 10.4 and 11.1‰ versus SMOC, with the only exception of the Fumarole Norte collected in November 2006 (−0.9‰ vs. SMOC). One gas sample (Fumarole NE, April 2004; ICT) was measured for the $^{40}Ar/^{36}Ar$ isotopic ratio, showing a value of 325 (Table 1), i.e. slightly higher than that of the air (295.5).

5 Discussion

5.1 Fumarole Migration and Discontinuous Monitoring Activity

This chapter was designed to assemble the chemical variations observed in a relatively large span of time (1998 to 2014), the relationships with the relatively few isotopic data available and the volcanic activity of Poás, particularly after the new phreatic phase that started in 2006 and still on-going and the Chinchona earthquake that occurred in January 2009. Owing to safety reasons, to the best of our knowledge, no chemical and isotopic data are available after 2014.

As reported by Vaselli et al. (2003), the fumarolic activity at Poás was characterized by a large spatial variability in terms of fumarolic vents, as they migrated and/or disappeared while in other cases new fumaroles formed. Consequently, maintaining one or more fumaroles as monitoring reference sites was practically impossible. The longest period of observation was reported for the Dome from where 29 and 5 gas samples were collected by ICT and AT, respectively, between 1999 and 2014, although, even in this case, the same sampling site was not always the same. In addition, from middle 2000 to 2007 no geochemical data are available for this fumarole.

In 1998, the Dome fumarole was too weak to be sampled and only a typical hydrothermal ($CO_2–H_2S$ dominated) gas was collected from Pared Sur that was not found in the 2000 sampling survey. Other fumaroles had a relatively short life, Fumarole Norte: from 2001 to 2008, and sampled by ITC from 2001 to 2004 and by AT up to 2009; La Niña: from 2001 to 2005; Fumarole NE: from 2001 to 2004; Fumarole Este: from 2001 to 2009. This implies that the opening of the 2006 phreatic episodes was better recorded by the NE and Este fumarole while the Dome can be considered a good proxy for evaluating the possible effects derived by the Cinchona earthquake. Another problem to be considered is when the data collected by AT and ICT are compared. Different periods of sampling, different sites from where a certain fumarole was collected and different techniques of sampling and analyses may be challenging to overlap the data despite the fact that they were likely sampled "more or less" from the same site. In addition, when new fumarolic vents open it was difficult to evaluate whether their chemical composition was to be considered chemically representative of the system since they were likely affected by hydrofracturing processes of chilled fragile margins at the surface due to volatile overpressure or uprising magma (e.g. Casertano et al. 1987; Rymer and Brown 1989; Rowe et al. 1992; Fischer et al. 2015). This means that the new fumaroles may likely need some time before reaching a steady-state status as shown by Fumarole NE (high concentrations of CO_2, SO_2 and H_2S, which from February to November 2001 dramatically decreased). A different behavior, though always indicating that few days-to-months (?) are necessary to stabilize a "young" fumarolic system, was shown by La Niña fumarole where SO_2 was not detected from February 2001 to February 2002 but appeared in

April 2002 (Table 1). During the very first sampling, this fumarole was indeed characterized by a small boiling pool that eventually dried out, thus resulting in the presence of acidic gases in April 2002. In any case, it is quite difficult in an active volcanic system such as that of Poás to attribute these initial variations and chemical modifications to the system itself or to the response of changing magmatic and hydrothermal conditions occurring at depth.

Fischer et al. (2015) examined the reactions that controlled the major components (H_2O, CO_2 and SO_2) of the Poás fumaroles, demonstrating that they were basically depending on chemical reactions of the gas phase, which involved the sulfur species at temperatures from 400 to 800 ° C, whereas the rock buffer appeared to have no control on the Poás gas chemistry. This important result allowed to consider the H_2S/SO_2 ratio as an indicative parameter of possible fluctuations related to modifications of the plumbing system. Similarly, volcanic variations can be assessed by the C/S_{tot} ratio as CO_2 and S are characterized by different solubility in silicate melts, the former being less soluble (e.g. Carroll and Webster 1994, Holloway and Blank 1994, Aiuppa et al. 2005, 2009; Fischer et al. 2015).

5.2 Time Variations in the Gas Chemistry at Poás Volcano

In this section, the temporal variations of the H_2/H_2O, H_2/Ar, CO/CO_2, CH_4/CO_2 and, HCl/HF log-ratios for selected fumaroles (i.e. Dome, Norte, Niña, Este, NE and Norte fumaroles) of Poás to evaluate the modifications of the plumbing magmatic/hydrothermal system that occurred at depth from 1998 to 2014 are taken into account. As previously mentioned, the fumarole collection was discontinuously carried out due to the fact that fumarole migration in time strongly affected the sampling activity. The temporal variation of the isotopic composition of helium was also considered whereas those of carbon, nitrogen, chlorine and argon were neglected due to the paucity of the data.

Fumaroles characterized by high temperatures in active volcanic systems are mainly dominated by H_2O, CO_2, SO_2 and H_2S with minor concentrations of H_2, HCl, HF and CO and traces of noble gases, e.g. helium and argon (Giggenbach 1996). Fluids emitted by volcanoes along convergent plates also show significant N_2 contents with respect to those from systems located in divergent and hot-spot geodynamic settings, due to the involvement of oceanic organic matter-rich sediments during subduction processes (i.e. Sano et al. 2001; Fischer et al. 2002). On the other hand, in addition to the rare gases, hydrothermal discharges are mostly consisting of H_2O, CO_2, H_2S and CH_4 and other reduced species, e.g. H_2 and CO, also indicative of high-temperature conditions, whereas HCl and HF are rarely detected (Giggenbach 1996). This implies that the magmatic systems may be considered to have a more oxidant character with respect to the hydrothermal systems where reduced conditions dominate. Poás fumaroles were mainly characterized by relatively low temperatures (<100 °C) where the presence of SO_2 was however recorded along with that of HCl and HF in most gas discharges, suggesting that the hydrothermal system was not able to completely scrub the most acidic gas species, likely due to the strong flux of the uprising magmatic gases and the proximity of the magma to the surface (about 500 m; Rymer and Brow 1989). Notwithstanding, the presence and the content of CH_4 and other gases species such as H_2, H_2S and CO suggest that the hydrothermal system modified the pristine composition of the magmatic gases. As a consequence, the selected ratios (e.g. H_2S/SO_2, CO/CO_2, CH_4/CO_2) can be considered representative the hydrothermal/magmatic ratio. On the other hand, the H_2/H_2O and H_2/Ar ratios are sensitive to heat pulse events from the magmatic source, since H_2O and Ar are related to the presence of a surficial component, i.e. the air saturated groundwater feeding the system (Giggenbach and Goguel 1989), whereas H_2 readily responds to changes of the temperature (similarly to CO) and redox conditions. Considering that F is more soluble in silicate melts than

Cl, the HCl/HF ratios can provide information on the degassing state of the magmatic body at the source of the fumarolic gases.

The temporal variations of the H_2S/SO_2 ratios (expressed as log) and that of the helium isotopic values are reported in Fig. 6. From 1999 to 2005, the $\log(H_2S/SO_2)$ ratios of most fumaroles were in a relatively narrow range (−2 to −1), excepting those of La Niña, which showed strong variations likely due to the presence/absence of condensed water at the surface or just below it, which governed the solubility of SO_2. In this period, a significant variability of the $\log(H_2S/SO_2)$ ratio was also shown by the Fumarole Este that can likely be attributed to the different sites from where the gas discharge was sampled even during a single sampling session (Table 1). From the beginning of 2005, the Fumarole Norte was characterized by a sharp increase in the $\log(H_2S/SO_2)$ ratio that reached +2 in middle 2005 whereas it decreased after the beginning of the phreatic events, suggesting a more efficient discharge of the magmatic component. The Fumarole Este also showed a similar behavior. At the end of 2008, the $\log(H_2S/SO_2)$ ratio of the Dome increased quite dramatically and after the Cinchona earthquake (January 2009), an abrupt decrease with respect to those measured in 1999–2000 was recorded, reaching its lowest value in middle 2009 (ca. –2.5). This is apparently suggesting that after the partial expulsion of the hydrothermal component, the magmatic/hydrothermal ratio increased. After 2009, the H_2S/SO_2 log-ratio started to progressively increase until 2014, likely due to the restoration of the hydrothermal system. Interestingly, the helium isotopic ratio did not show any significant variation and clustered around the value of 7 with the highest value recorded in 2004 (Fig. 6).

The $\log H_2/H_2O$ ratio with time is reported in Fig. 7. The values recorded at the Dome were higher than those recorded in the other fumaroles (>−3 and down to −6.4, respectively), although they were sampled in different periods. The trends depicted by the Norte, La Niña, Este and NE fumaroles do not appear to have a clear behavior. However, the Fumarole Este showed a decrease of the $\log(H_2/H_2O)$ ratio after the end of

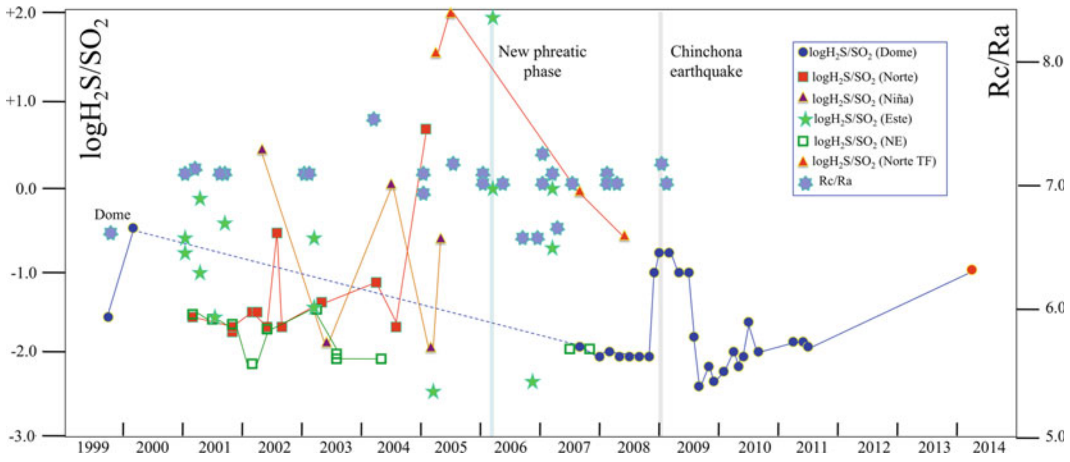

Fig. 6 Temporal variations of the $\log(H_2S/SO_2)$ ratio and the helium isotopic ratio (expressed as Rc/Ra, where Rc is the measured value corrected for the He/Ne ratio and Ra is that of the air) in selected fumaroles from Poás. The Dome is represented by blue (Vaselli et al. 2003 and unpublished data) and red (Fischer et al. 2015) circles; red squares and red triangles refer to the Fumarole Norte (Vaselli et al. 2003) and unpublished data and Fischer et al. (2015; Norte TF), respectively; the white green-bordered squares and the brown triangles represent the NE and Niña fumaroles, respectively, and the green stars indicate the Fumarole Este of Fischer et al. (2015; Este). A line connecting the Fumarole Este data was not drawn since they refer to different analyses carried out in the surroundings of such a fumarole; the blue seven-pointed stars depict the temporal variations of the helium isotopes. The renewed phreatic activity (March 2006) and the Cinchona earthquake are also indicated with light blue and light grey bars, respectively

2001, whereas from 2003 to 2007, no significant variations were recorded. The Fumarole Norte, after a progressive decrease of the log(H_2/H_2O) ratio from early 2001 to 2003, started to increase and before the phreatic activity in 2006 a sharp increase was recorded. This may suggest an efficient heat pulse by the magma chamber, although a similar behavior was not recorded by the other fumaroles. In 2007 the log(H_2/H_2O) ratio of the Dome was around −3 and then, it reached about −1.5 in correspondence of the Cinchona seismic event. Afterward, a significant decrease occurred at middle 2009. Subsequently, the log(H_2/H_2O) ratio increased sharply and in less than one year the log-ratios were higher than −1 and remained relatively stable up to the end of 2011, suggesting that well before the Cinchona earthquake the activity of Poás was affected by either an increasing heat pulse induced by magmatic source or an increasing hydrofracturation. It is to remark that the log(H_2/H_2O) ratios were in most cases significantly higher than that suggested by Giggenbach (1991) for hydrothermal volcanic systems [log(H_2/H_2O) = −2.8], indicating disequilibrium conditions related to water dissociation (e.g. Martini 1993). In 2014, the log(H_2/H_2O) ratio at the Dome was similar to that recorded in 1999 (ca. −3).

The trends of the log(H_2/Ar) ratios are reported in Fig. 8. The Dome was characterized by higher log(H_2/H_2O) values than those recorded at the other fumaroles, although no temporal overlapping measurements were carried out. Fumarole NE only approached log(H_2/Ar) ratios comparable to those of the Dome in 2007. From 2001 to 2005 the Fumarole Norte showed H_2/Ar log-ratios lower than 1.7; in correspondence of the 2006 phreatic activity a value approaching 2 was recorded. Then, it decreased to −1.6 and resumed up slightly lower than 0 in 2008 before the earthquake that stroke Cinchona. The Dome in 1999 and 2000 showed values of the log(H_2/Ar) ratios similar to those of the other fumaroles. In 2007, the log-ratio was almost 3 and increased up to 3.5 at the beginning of 2009 and after a sharp decrease, the log(H_2/Ar) ratio started to increase similarly to what recorded by the log (H_2/H_2O) ratio and values up to 5 were reached whereas in 2014, the log-ratio was slightly higher than 3. Basically, the behavior of the log(H_2/Ar) ratio intimately mimics that registered by the

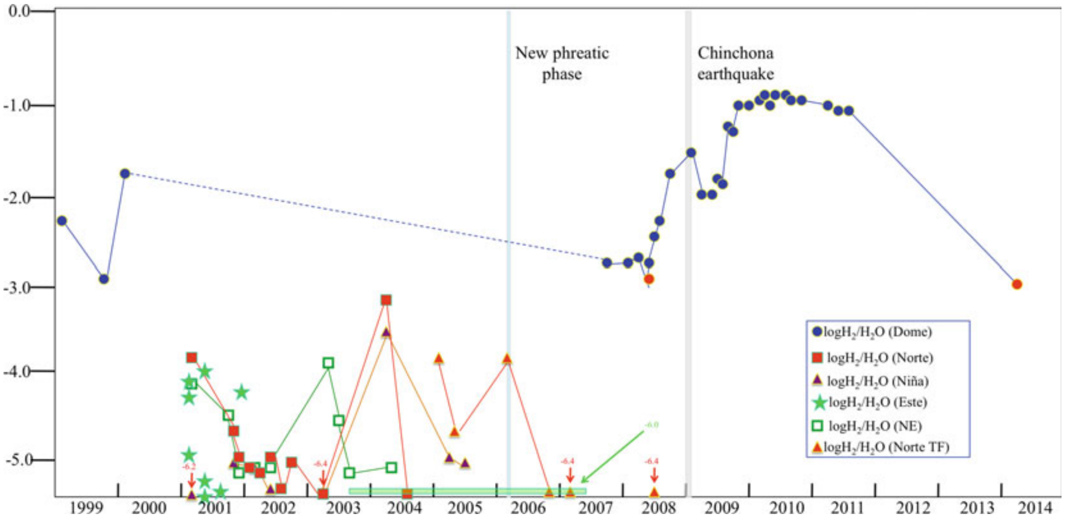

Fig. 7 Temporal variations of the log(H_2/H_2O) ratio in selected fumaroles from Poás. Symbols as in Fig. 6

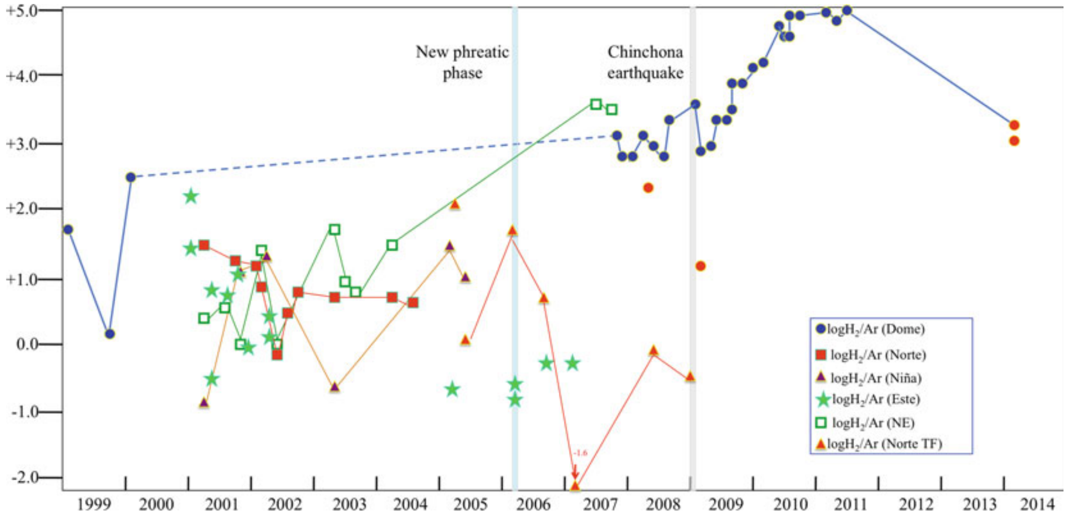

Fig. 8 Temporal variations of the log(H_2/Ar) ratio in selected fumaroles from Poás. Symbols as in Fig. 6

H_2/H_2O log-ratio, indicating an over-production of H_2 produced by H_2O thermal dissociation.

A similar picture can be observed when the CO/CO_2 log-ratios are considered (Fig. 9), carbon monoxide being more representative of a reduced (hydrothermal) environment. Most of the fumarolic gas discharges sampled from 1999 to 2006 have log(CO/CO_2) values between −6.5 and −4.0, although in 2003 a slight increase of the log(CO/CO_2) values was recorded for most fumaroles with the exception of the Dome where no data were available. As shown by the log(H_2/H_2O) and log(H_2/Ar) ratios, at the Dome those of log(CO/CO_2) are characterized by a significant increase at the beginning of 2007. From early 2008 to early 2009 the log(CO/CO_2) values steadily increased (ca. −3), preceding the further increase in this log-ratio a few months after the Cinchona earthquake. Subsequently, at the end of 2009 the log(CO/CO_2) ratio resumed by approaching −2. Eventually, in 2014 a clear drop was registered. Basically, carbon monoxide is indicative of high temperatures and tends to re-equilibrate relatively quickly.

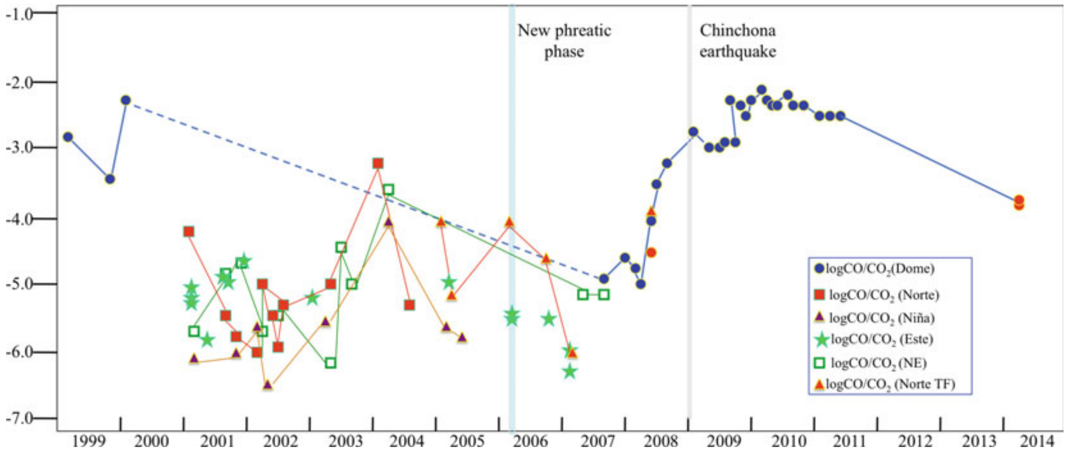

Fig. 9 Temporal variations of the $logCO/CO_2$ ratio in selected fumaroles from Poás. Symbols as in Fig. 6

In Fig. 10, the temporal variations of the log (CH_4/CO_2) ratios are reported. The behavior of this log-ratio refers to a hydrothermal component (CH_4) compared with CO_2 that better represents a magmatic signature, as also testified by the carbon isotopic values (Table 1). Consequently, the trends observed for the selected fumaroles of Poás strictly mimic those observed for the log (H_2S/SO_2) ratio (Fig. 6). This is particularly evident when the temporal variations recorded for the Dome are considered. In 1999–2000, the log(CH_4/CO_2) values were indeed the highest ones among all the considered dataset (up to −4), indicating that the hydrothermal component was dominating. Lower values were observed by the other fumaroles, though not sampled in the same period, which however showed an increasing trend from 2001 to 2005, few months before the renewed phreatic activity (ca. −3.5, Fumarole Norte). In 2007, the Dome was characterized by a log(CH_4/CO_2) ratio slightly lower than −6 and increased in early 2008. Then, a sharp decrease was recorded up to middle 2008. After the Cinchona event a dramatic increase of the log(CH_4/CO_2) ratio was observed that subsequently decreased down to −8.3 in 2010, supporting the presence of a magmatic component that was dominating over the hydrothermal one. In 2011 and in 2014, the log (CH_4/CO_2) recovered and reached the value showed in early 2009.

Eventually, the log(HCl/HF) ratio versus time is plotted in Fig. 11. As already mentioned, the HCl/HF log-ratio is a useful parameter to evaluate either increasing magmatic/hydrothermal ratio or increasing magma degassing. The Norte, La Niña, Este and NE fumaroles from 2001 to 2007 (when the last sample from the NE fumarole was collected), though not collected in the same periods, showed higher HCl/HF log-ratios that those recorded at the Dome, with the exception of the Fumarole Norte from the second half of 2002 to early 2003, when the log-ratios were about 0.5. The trends showed by CH_4/CO_2 and H_2S/SO_2 log-ratios at the Dome are similar to those of the HCl/HF log-ratio. The chlorine isotopes measured in several fumarolic gas discharges are not helpful in defining whether Cl is pristine, being affected by removal (distillation) of $H^{35}Cl$ from steam as Cl^-_{aq} in water (e.g. Sharp et al. 2010; Fischer et al. 2015), as supported by the high $\delta^{37}Cl$ values recorded at Poás (Table 1), although the Fumarole Norte, collected in 2006 approached the mantle value (−1.6‰; Bonifacie et al. 2008). From the end of 2003, all the fumaroles from Poás, showed a decreasing trend of log (HCl/HF) ratio that reached the lowest value at

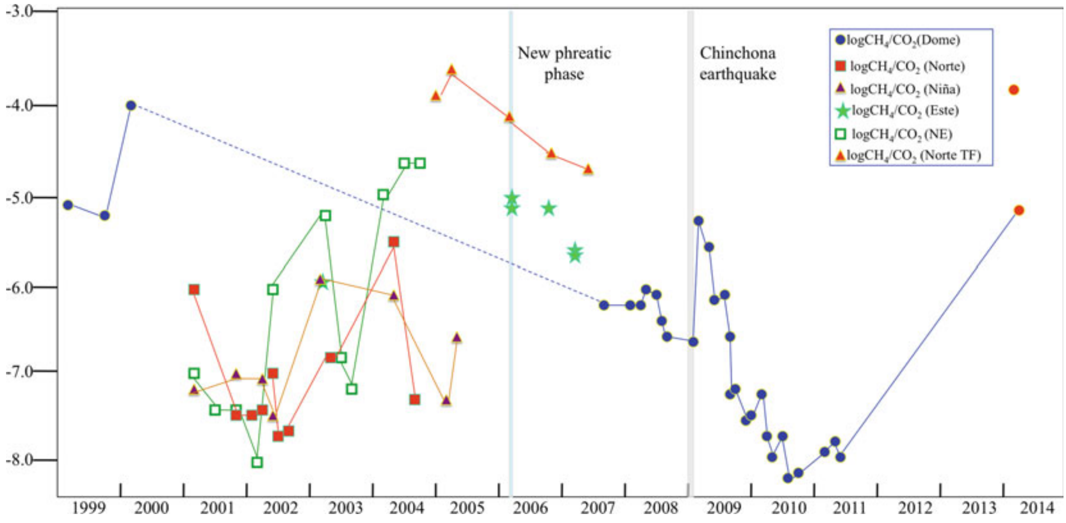

Fig. 10 Temporal variations of the log(CH_4/CO_2) ratio in selected fumaroles from Poás. Symbols as in Fig. 6

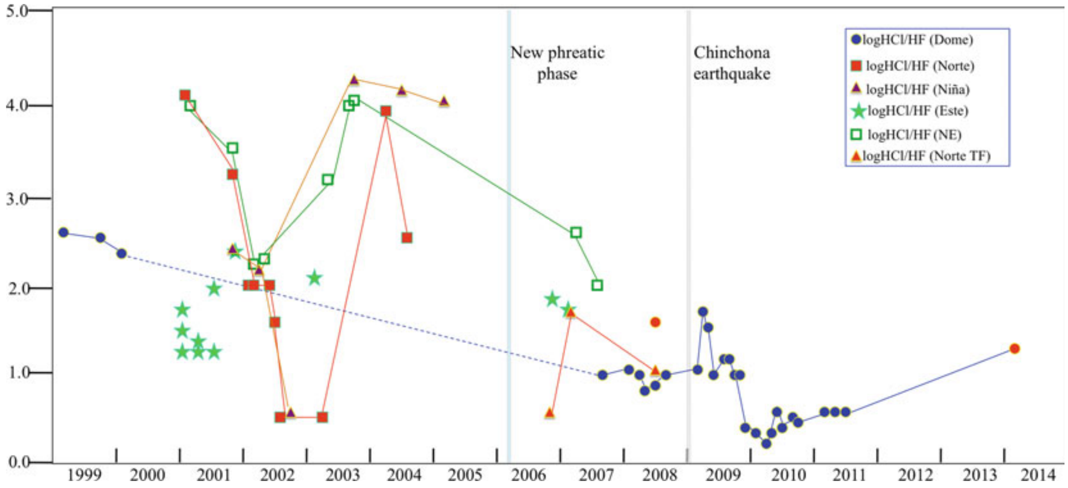

Fig. 11 Temporal variations of the log(HCl/HF) ratio in selected fumaroles from Poás. Symbols as in Fig. 6

the Fumarole Norte in November 2006 when the most primitive δ^{37}Cl value was measured. From middle 2007 to early 2009, the Dome showed a relatively constant log(HCl/HF) value that dramatically increased after the Cinchona earthquake. Then, the log-ratio started to progressively decrease up to early 2010. Subsequently, up to 2014 it constantly increased when a value slightly higher of 1 was achieved.

6 Summary and the Renewal Activity

The fumarolic activity from 1998 to 2014 at Poás was affected by strong modifications. In 1998 the fumarolic activity at Poás was relatively quiet and mainly concentrated at the interface between the pyroclastic dome and the acidic lake, whereas sporadic gas discharges were distributed throughout the inner crater with temperature never exceeding that of boiling water. From 1999 to 2000 the Dome fumarole was persisting and new fumarolic vents, not sampled, formed in the inner NE and E sectors of the crater. Despite the relatively low outlet fumarolic temperatures, concentrations of magmatic gases, such as SO_2, HCl and HF, were abundant. Significant modifications of the fumarolic fields were recorded up to 2006 (when a new phase of phreatic activity took place), although in 2005 the lake level started to decline and sub-lacustrine fumaroles turned vigorous. In 2001 the lake depth was 41 m deep (Vaselli et al. 2003), and a record level in early 2005 was achieved when the eastern bottom of the crater was over-flooded, and dropped down to 10 m in 2014 (Fischer et al. 2015; Martínez et al. Chapter "Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights Into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles" and references therein; Rouwet et al. Chapter "39 Years of Geochemical Monitoring of Laguna Caliente Crater Lake, Poás: Patterns from the Past as Keys for the Future"), approaching the 1989–1994 period when the lake dried out completely.

The discontinuous measurements of the fumarolic gas discharges at Poás has highlighted that: (a) useful insights inside the dynamics of the hydrothermal/magmatic system were mostly obtained by the Dome for which the geochemical record was relatively long and consistent. Nevertheless, from 2001 to 2007 no data are available and consequently, the possible geochemical variability of the gas composition prior and after the onset of the phreatic activity in 2006 was not recorded. However, the geochemical data collected for the Fumarole Norte registered an increase of the hydrothermal-related parameters (e.g. increase of the H_2S/SO_2, CO/CO_2, and

CH_4/CO_2 ratios). No data were available for this fumarole after 2008; (b) the Poás fumaroles suffered strong modifications from 1998 and time migration of the gas vents prevented the possibility of long-term gas sampling and consequently, a detailed reconstruction of the evolution of the hydrothermal/magmatic system was not allowed; (c) opening, closing and shifting of the fumarolic discharges are interesting aspects that should be investigated in more detail. As previously mentioned, the opening of a new fracture that produces a fumarolic discharge is not apparently reflecting the real chemical composition of the plumbing system since several days-to-months may be needed before a steady state status is achieved. This was particularly evident for La Niña fumarole that showed an up-and-down variation for most of the considered geochemical parameters (see Figs. 6–11) from the end of 2001 to the beginning of 2005, when it basically disappeared.

According to Vaselli et al. (2003), Fischer et al. (2015) and this work, the modifications suffered by the hydrothermal-magmatic system of Poás can be summarized in Fig. 12. Fischer et al. (2015) and Rymer et al. Chapter "(Geophysical and Geochemical Precursors to Changes in Activity at Poás Volcano" and references therein) suggested that a magma injection possibly occurred in late 2000-early 2001 on the basis of geochemical and gravity data, respectively, although on the behavior of polythionates Martínez et al. Chapter "Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights Into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles" and references therein) suggested the injection of fresh magma earlier (1996–1999). This implies that the chemical composition of the fumarolic gases and the changes observed from 1998 to 2014 are likely resulting by combined effects at different degrees of interaction between the magmatic and hydrothermal system and the acidic lake. Basically, from 1998 onwards the volcanic plumbing system of Poás passed from hydrothermal(magmatic)-dominated to magmatic-dominated conditions well before the Cinchona earthquake. It may speculate that the Cinchona event favored the (partial) removal of the hydrothermal system that slowly recovered until when the new eruptive phase (more violent than that commenced in 2006) took place in 2017. Injection of new and undegassed magma, heating of the hydrothermal system and gas pressure build-up, and hydrofracturing through or the rupture of the alteration-sealing cap-rock through 2005–2006

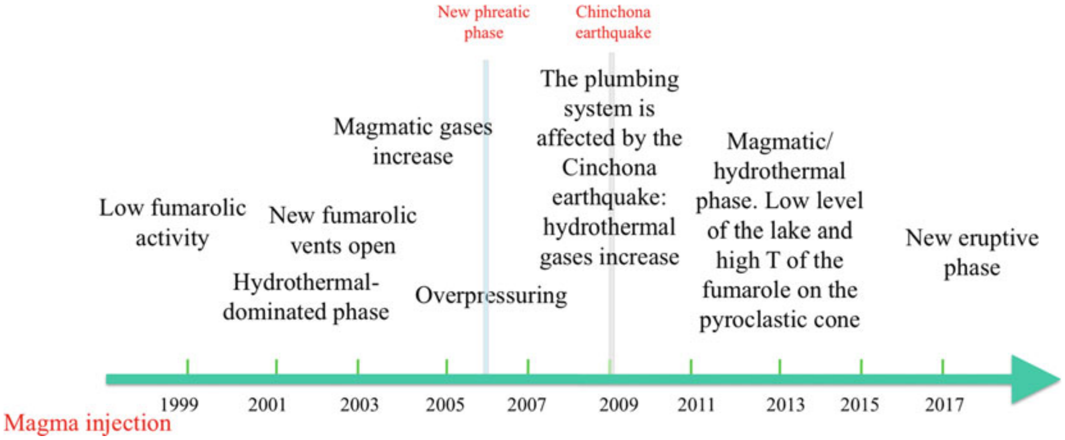

Fig. 12 Schematic diagram summarizing the most significant processes suffered by the Poás hydrothermal-magmatic system

were likely the main processes that affected the magmatic-hydrothermal system of Poás.

In late March 2017, seismic activity, ground deformation, CO_2/SO_2 ratios of the gases from the dome and the lake, lake temperature, acidity and ion composition increased significantly and sharply. In early April 2017, the lake level rose rapidly up to 2 m in two weeks, despite the scarce precipitations. Also, a 4 m wide new boiling mud-pool ("borbollón") (Fig. 13a; e.g. Martínez et al. Chapter "Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights Into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles" and references therein) appeared at the bottom of the crater about 100 m SE the pyroclastic dome. The fumarolic activity at the Dome fumarole increased, new fumaroles formed in the central and western sectors of the dome and some gas bubbling and steam were observed at the interface between the acidic lake and the dome, turning the lake grey and full of floating sulfur (Fig. 13b). On the 12th of April, the phreatic activity resumed and destroyed ca. 10% of the central part of the dome. The boiling mud-pool disappeared. The phreatic activity became more intense and at the end of April phreato-magmatic eruptions were recorded. In May, the repeatedly eruptive events destroyed ca. 90% of the pyroclastic dome structure. Eventually, the lake dried out completely, allowing the direct release of the fumarolic gases to the atmosphere visible (Fig. 13c), since they

Fig. 13 **a** The new mud boiling pool, a (crystobalite-rich) "borbollón" that opened in April 2017, 200 m behind the pyroclastic dome; **b** The Poás lake in April 2017 with strong upwelling; **c** the Poás lake disappeared in May 2017 showing high-temperature fumaroles around the areas occupied by the pyroclastic dome (Boca A o Boca Roja)

were previously discharging into the Laguna Caliente. Unfortunately, the hostile and dangerous environment prevented regular direct geochemical sampling. Nevertheless, once the still on-going volcanic activity will be over, gas sampling should be carried out as fast and often as possible in order to verify whether the pre-eruptive conditions are to be restored and the geochemical behavior of the remaining or new fumaroles.

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