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Chemical evolution and volcanic activity of the active crater lake of Poás volcano, Costa Rica, 1993–1997

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Abstract

Concentrations of chloride and sulfate and pH in the hot crater lake (Laguna Caliente) at Poás volcano and in acid rain varied over the period 1993–1997. These parameters are related to changes in lake volume and temperature, and changes in summit seismicity and fumarole activity beneath the active crater. During this period, lake level increased from near zero to its highest level since 1953, lake temperature declined from a maximum value of 70°C to a minimum value of 25°C, and pH of the lake water increased from near zero to 1.8. In May 1993 when the lake was nearly dry, chloride and sulfate concentrations in the lake water reached 85,400 and 91,000 mg l^{-1}, respectively. Minimum concentrations of chloride and sulfate after the lake refilled to its maximum volume were 2630 and 4060 mg l^{-1}, respectively. Between January 1993 and May 1995, most fumarolic activity was focused through the bottom of the lake. After May 1995, fumarolic discharge through the bottom of the lake declined and reappeared outside the lake within the main crater area. The appearance of new fumaroles on the composite pyroclastic cone coincided with a dramatic decrease in type B seismicity after January 1996. Between May 1995 and December 1997, enhanced periods of type A seismicity and episodes of harmonic tremor were associated with an increase in the number of fumaroles and the intensity of degassing on the composite pyroclastic cone adjacent to the crater lake. Increases in summit seismic activity (type A, B and harmonic tremor) and in the height of eruption plumes through the lake bottom are associated with a period of enhanced volcanic activity during April–September 1994. At this time, visual observations and remote fumarole temperature measurements suggest an increase in the flux of heat and gases discharged through the bottom of the crater lake, possibly related to renewed magma ascent beneath the active crater. A similar period of enhanced seismic activity that occurred between August 1995 and January 1996, apparently caused fracturing of sealed fumarole conduits beneath the composite pyroclastic cone allowing the focus of fumarolic degassing to migrate from beneath the lake back to the 1953–1955 cone. Changes in the chemistry of summit acid rain are correlated changes in volcanic activity regardless of whether fumaroles are discharging into the lake or are discharging directly into the atmosphere.

Keywords: crater lakes; fumaroles; seismicity; chloride; sulfate; acid rain; environmental impact; Poás volcano

1. Introduction

Crater lakes in active volcanoes are dynamic systems. They interact with cooling shallow magma bodies and/or magmatic–hydrothermal systems beneath them. Changes in heat flow and degassing rates induce variations in the chemical and physical

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properties of crater lakes. Changes in these properties provide the basis for volcano monitoring programs assuming that external influences (e.g. rainfall and lake-sediment interaction) can be isolated. Crater-lake geochemistry related to volcanic activity can be an important tool to predict and monitor volcanic events, especially when combined with other geophysical techniques such as seismic or deformation studies. In addition, crater lakes can be the source of increased volcanic hazards (i.e. lahars, atmospheric pollution, seepage of toxic fluids, e.g. Pasternack and Varekamp, 1997), so their activity needs to be carefully studied through volcano monitoring programs. Fortunately, reports from several well-studied crater lakes on active volcanoes are available, e.g. Kusatsu–Shirane volcano, Japan (Takano, 1987; Takano and Watanuki, 1990; Takano et al., 1994a); Ruapehu volcano, New Zealand (Takano et al., 1994b); Kelut volcano, Java (Badrudin, 1994) and Laguna Caliente, Poás. The latter crater lake has been studied by Racci-chini and Bennett (1977), Brantley et al. (1987), Brown et al. (1989, 1991), Rowe et al. (1992a,b, 1995), Rowe (1994) and Rymer et al. (2000 – this volume).

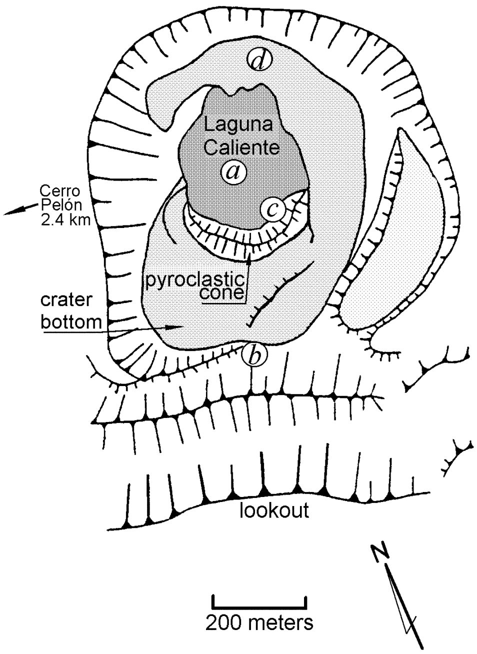

Fig. 1. Map of the main crater of Poás Volcano, indicating the location of the areas with intense fumarolic discharge observed from 1993 to 1997: (a) from January 1993 to May 1995, subaqueous fumarolic activity predominated at Laguna Caliente ; (b) then the main fumarolic activity migrated to the southern wall of the crater in May, 1995; (c) finally, after January 1996, the locus of most fumarolic activity was centred on the pyroclastic cone formed between 1953–1955. (d) low-temperature fumaroles formed on the 80-m-long, NE-trending fracture, that appeared on the northern terrace in April, 1997. Cerro Pelón, the acid rain sampling site, is located 2.4 km southwest from Laguna Caliente. Map adapted from Rymer et al., 2000 – this volume.

2. Poás volcano

Poás volcano is one of the most active volcanoes of Costa Rica and is approximately 35 km northwest of San José, in the Central Cordillera of Costa Rica (10°12′00″N and 84°13′58″W, 2708 m above sea level). It is a broad well-vegetated basaltic-andesite strato volcano, with a summit area that contains three cones and the eroded remnants of two elongate calderas (Prosser and Carr, 1987). The active cone contains a crater lake, Laguna Caliente (Fig. 1), which is located between the two older cones: the von Frantzius cone to the north and the Botos cone, which contains a freshwater lake at its summit, to the south (Fig. 6). Radiocarbon dating of pyroclastic deposits associated with the last lava flow eruption by the Botos cone gives an age of 7540 ± 100 years old (Prosser, 1985).

Laguna Caliente is a hot, extremely acidic, crater lake filled with a concentrated chloride–sulfate brine rich in rock-forming elements and fine native sulfur particles. According to the physico-chemical classification scheme for volcanic lakes of Pasternack and Varekamp (1997) Laguna Caliente was a hot acid hyperbrine volcanic lake from 1984 to 1990. During this period, lake temperature ranged from 38 to 96°C, pH ranged from −0.87 to 0.26 and total dissolved solids (TDS) ranged from 60 to 360 g kg^{-1} (Rowe et al., 1992a). Maximum concentrations of chloride and sulfate in samples of lake brine collected prior to the lake's initial disappearance in early 1989 were 120,000 and 286,000 mg kg^{-1}, respectively (Rowe et al., 1992a). The temperature and extreme fluid chemistry observed in the crater lake were caused by the combined effects of subaqueous fumaroles discharging steam and magmatic gases into the bottom of the lake and intense evaporation at the surface of the hot lake.

The active crater hosts an active hydrothermal system (Casertano et al., 1987) supplied with heat and volatiles by a small, shallow magma body whose upper surface is believed to be within 500 m of the crater floor (Rymer and Brown, 1989). Annual rainfall in the vicinity of the active crater is approximately 3.5 m per year (Liao, 1997) with the dry season from January to mid-May. The volume, temperature and water chemistry of Laguna Caliente vary considerably, responding to changes in rainfall, thermal power output and summit seismic activity (Brown et al., 1989, 1991; Rowe et al., 1992a,b).

2.1. Summary of historical activity

Historical activity at Poás with reports of fumarolic activity, vapour eruptions and phreatic explosions since 1828 are summarised by Krushensky and Escalante (1967), Raccichini and Bennett (1977), Vargas (1979), Boza and Mendoza (1981), Malavassi and Barquero (1982) and Malavassi et al. (1993). The largest reported eruption occurred on 25 January 1910, when a large steam and ash cloud reached 4–8 km above the summit. During this eruption most of the crater lake was ejected, but the lake did not completely disappear (Calvert and Calvert, 1917).

From 1910 to 1952, the crater lake was present and nearly continuous fumarolic activity was observed in the active crater. Activity at the volcano changed markedly in 1952 when geyser-like phreatic eruptions through the crater lake returned, marking the onset of a period of phreato-magmatic activity that would continue for several years. Two vents were active at Poás' main crater during this eruption cycle: one that formed a small composite pyroclastic cone 40 m high was formed in the central part of the active crater, and another unnamed vent that formed about 150 m to the north of the pyroclastic cone. The northern vent collapsed and later filled with water to form Laguna Caliente. By 1961, the crater lake had reformed with intermittent geyser-like phreatic eruptions, e.g. in 1977–1980, phreatic eruptions occurred with column heights from several metres to 2 km and a phreatic explosion in 1978 erupted large sulfur-encrusted blocks (Bennett and Raccichini, 1978a,b; Bennett, 1979; Francis et al., 1980).

Intense swarms of type A earthquakes were recorded beneath the active crater in July 1980. These swarms are believed to represent hydrofracturing of the chilled, brittle margin of the shallow magma body beneath the crater (Casertano et al., 1987). Following the type A swarms, a very dramatic change occurred in January 1981 when high-temperature fumaroles (up to 925°C) appeared on the pyroclastic cone and gas columns rose up to 2 km high. At the same time, phreatic eruptions ceased to occur at Laguna Caliente (Barquero and Malavassi, 1981a,b, 1982, 1983). The temperature of fumaroles on the pyroclastic cone gradually decreased from 960°C in mid-1981 to 441°C in 1987 (Barquero and Fernández, 1988) and were reduced to boiling and sub-boiling point temperatures by 1989 (Smithsonian Institution, 1989). The annual number of type B earthquakes was 12,000 in 1983 (Fernández, 1990). Tremor hours were high (1250–1800 h) during 1981–1982 when high-temperature degassing was concentrated on the pyroclastic cone. The pyroclastic cone remained the site of obvious fumarolic activity until June 1987 when geyser-like eruptions returned to Laguna Caliente.

A swarm of type A earthquakes, representing either a small episode of renewed magma ascent or another less extensive hydrofracturing event, occurred between February and May 1986 (Rymer and Brown, 1989; Rowe et al., 1992b). Phreatic eruption columns reached 1 km in elevation on 9 April 1988 and expelled lake sediments fell 0.5 km south of the crater rim. Water temperatures of Laguna Caliente increased from 58 to 70°C in 1988. Type B earthquakes gradually increased from 12,000 per year in 1983 to over 100,000 per year in 1988. As the lake disappeared, lake-bottom fumaroles began to degas directly into the atmosphere so that direct emissions of the acid gases SO_2, H_2S, HCl and HF began to affect large areas west and southwest of the active crater. Areas affected by acid deposition extended up to 15 km southwest of the active crater; when the lake is present, acid deposition is typically restricted to areas 3 km or less downwind of the active crater (Barquero and Fernández, 1990; Fernández et al., 1994). The level of Laguna Caliente dropped drastically during 1988 and the lake disappeared completely in April 1989. After the lake disappeared, steam jets lifted lake sediments into the air and periods of harmonic tremors reappeared. On 1 May 1989, unusually powerful steam jets ejected lake sediments 1–2 km into the air; these sediments later fell

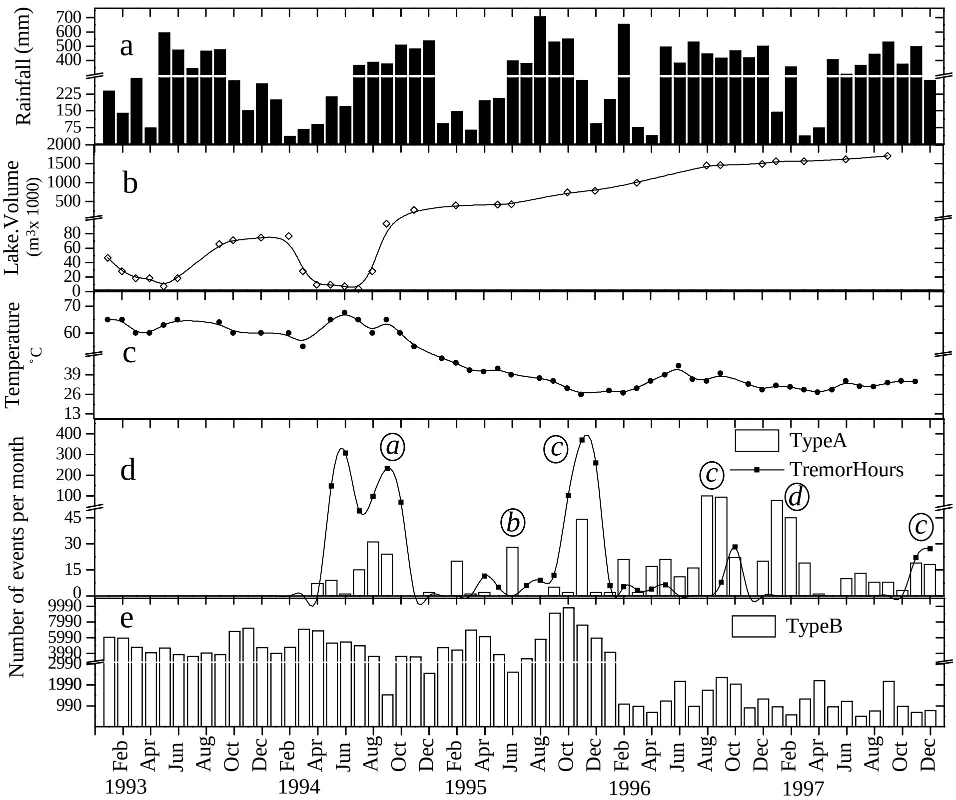

Fig. 2. Monthly variation of physical parameters related to Laguna Caliente (1993–1997) including: (a) rainfall at the summit of Poás Volcano; (b) crater lake volume; (c) crater lake water temperature; (d) summit seismicity recorded at POA2 seismographic station: Type A seismicity and tremor hours, and (e) Type B seismicity. On Fig. 2d, encircled a, b, c and d, refers to the location of fumaroles and their forming events shown in Fig. 1.

on populated areas 18 km southwest of the volcano. Dry ash and steam eruptions continued intermittently for three weeks with plume heights ranging between 1.5–2 km (Smithsonian Institution, 1989).

Boiling brine pools, mud pots and sulfur volcanoes up to three metres high were formed on the crater's floor. Pits filled with molten sulfur at temperatures of 140°C were also observed on the lake bottom at this time (Oppenheimer and Stevenson, 1989). Reddish flames believed to represent the combustion of native sulfur were observed around the vents of high-temperature fumaroles on the lake floor suggesting temperatures >400°C. Lake desiccation and subsequent refilling occurred during each dry season between 1989 and 1992.

Phreatic eruptions resumed in March 1990 and a strong eruption in April 1990 followed a swarm of type A earthquakes that occurred at Poás six hours after the 25 March 1990 subduction zone earthquake ($M_w = 7.0$, Protti et al., 1995), with an epicentre offshore of the Nicoya Gulf, 170 km southwest of Poás volcano. Dry steam and ash eruptions, similar to those that occurred in May 1989, resumed in May 1990 when the lake again disappeared (Smithsonian Institution, 1990). Type B earthquakes that had peaked at greater than 100,000 per year in 1988, continued to show similar yearly totals during 1989–1991. Lake-water temperatures during the rainy months (May–December) varied between 63 and 71°C in 1991, and then averaged around 70°C in 1992 and 55°C in 1993. Estimated maximum depth of the lake during the rainy season of 1991 was about three metres. This depth was attained again during the rainy season of 1992 and increased to an estimated six metres in 1993 (Smithsonian Institution, 1991, 1992, 1993).

3. Methods

3.1. Lake volume and depth

Volume and depth of Laguna Caliente were calculated from 30 sets of measurements of the dry lake basin geometry made with a precision theodolite and a distance-metre between August 1994 and September 1997 (Fig. 2b). Prior to August 1994, the depth and volume were estimated using field documentation. Changes in the diameter and volume of the lake were calculated using consecutive differences in water level (depth) and a geometric model of the lake that assumes an inverted, flat-bottomed cone [$V = \pi h(R^2 + r^2 + Rr)/3$ where R is the large radius, r the small radius, h the differential water level]. The error introduced by the difference between the geometric model and the curved shape of the actual lake bottom is estimated to be less than 5%.

3.2. Seismic data

Seismic data for the summit region of Poás Volcano were recorded from the POA2 seismographic station which is about 2.8 km southwest of Laguna Caliente at an elevation of 2500 m above sea level. The POA2 station is a telemetric station equipped with a Ranger SS-1 vertical, short-period seismometer (1 Hz). Seismic activity at Poás has traditionally been classified following the categories defined by Minakami (1969): (1) type A events are high-frequency events ($f >$ 3.0 Hz); (2) type B earthquakes are low-frequency events ($f <$ 3.0 Hz); and (3) periods of harmonic tremor ($f =$ 2.0–3.0 Hz). The latter are reported as the number of hours of tremor recorded per month.

3.3. Sampling and analytical methods

Lake temperature was measured using a thermocouple. Water samples were collected at two sites (north and south) twice a month along the lake shore using dark high-density polyethylene bottles that were stored at room temperature. Subsequent analysis of the sample collected from the north and south sides of the lake revealed pH, chloride and sulfate concentrations that were identical within analytical error indicating that the lake was well-mixed at the time of sampling because of thermal convection (Brantley et al., 1987). Lake-water samples were not filtered or diluted in the field. Data reported for the period late April to mid-August 1994 are based on samples collected from small temporal pools that formed after heavy rains on the dry lake bottom. The chemistry of these pools has been shown to be highly variable (Rowe, 1994), however, data for samples collected from these pools are included here for completeness. Rainwater samples were collected at Cerro Pelón twice a month at a site approximately 2.4 km southwest (i.e. downwind) of the active crater (Figs. 1 and 6). Rainwater samples were collected in high-density polyethylene bottles and were stored at 5°C to minimise the growth of bacteria or algae.

All the samples were analysed for pH, chloride and sulfate. Determinations of pH were done on unfiltered samples in the laboratory using a Corning potentiometer Model 10 with a relative precision of ±0.1 pH units. To determine the chloride and sulfate, samples were filtered with 0.2 μm pore diameter polycarbonate filters and analysed by ion chromatography on a Shimadzu HIC6A ion chromatograph that had a Shimpak ICA1 anionic exchange resin column and a Shimadzu CDD6A conductivity detector. A 2.5 mM phthalic acid and 2.4 mM Tris-(hydroxi-methyl) amino-methane (pH 4.0) solution was used as mobile phase. The chromatograph operated at 40°C with a flow-rate of 2.0 ml min^{-1}, in a range of measure of 0.1 mS cm^{-1}. Concentrations of chloride and sulfate were calculated by peak heights calibrated against a set of known standards. Analytical errors of the ion chromatography analyses are estimated to be ±5% for sulfate and ±10% for chloride.

4. Results

From 1993 to 1997, annual rainfall in the vicinity of the crater ranged from 3.8 to 4.6 m per year which is 9–33% above the long-term average of 3.5 m per year (Fig. 2a). The only exception was during 1994 when total annual rainfall in the summit area was just below the long-term average (~3.4 m).

Volume of Laguna Caliente varied from an estimated 3.7×10^3 to 1.7×10^6 m^3 between 1993 and 1997 (Fig. 2b). The volume decreased abruptly during the dry seasons of 1993 and 1994, but no significant volume changes were observed during the dry seasons

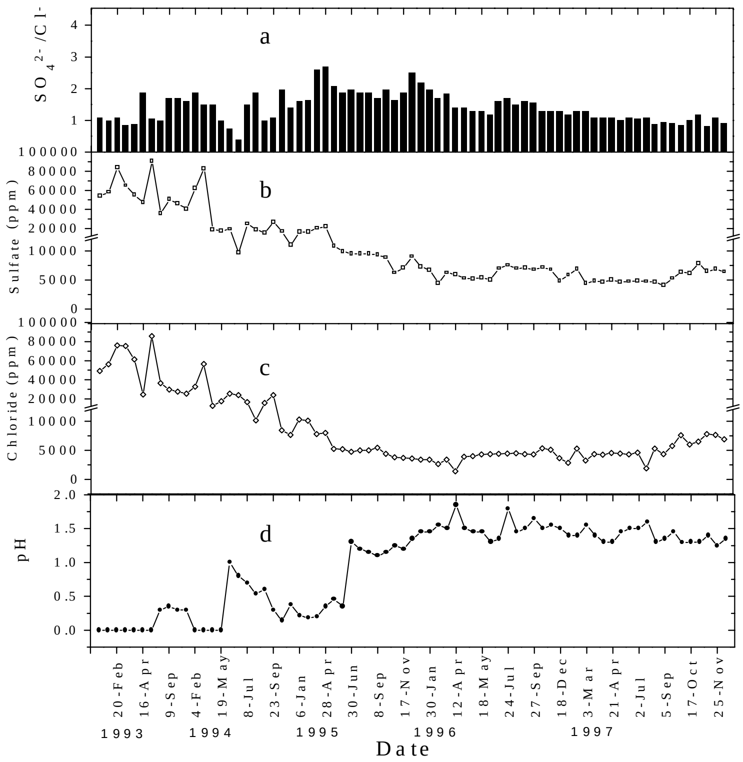

Fig. 3. Monthly variation of chemical parameters in water from Laguna Caliente (1993–1997) including: (a) SO_4^{2-}/Cl^- concentration ratios; (b) sulfate concentration; (c) chloride concentration, and (d) pH.

of 1995–1997. The mild increase in the slope of the volume curve recorded from June 1995 to August 1996 (Smithsonian Institution, 1996a) is associated with a period of above-average rainfall at that time (Fig. 2a,b). The temperature of the crater lake ranged from 25 to 70°C between 1993 and 1997 (Fig. 2c).

From January 1993 to January 1996, type B seismicity was extremely high in comparison with the seismicity recorded from February 1996 to December 1997. Monthly totals of type B earthquakes ranged from 1100 to 9839 during this period. An increase in the number of type B earthquakes in March–April 1994 is related to an increase in the lake-water temperature (Fig. 2c,e), with increases in the concentration of sulfate and chloride in lake water (Fig. 3b,c), and with the return of harmonic tremor and type A seismic events (Fig. 2d). Note that neither harmonic tremor or type A seismic events were observed at this time in 1993.

A minimum in the total number of type B earthquakes occurred in September 1994 after the enhanced period of volcanic activity and the lake began to reform (Fig. 2b,e). Increases in monthly total type B events (5960–9149) and harmonic tremor hours (12–370 h) occurred between September and December 1995. An increase in the number of type A earthquakes was also observed in November 1995 (44 events, Fig. 2d,e). However, sulfate and chloride concentration and lake-water temperature did not change in response to the increased seismicity recorded over this time period. Similarly, increases in the frequency of type B events were noted in October–November 1993 (6360 events), and in March–April 1995 (6995 events) without any obvious changes in lake temperature, lake volume, or concentrations of chloride or sulfate. During October–November 1993, type A and tremor seismicity were absent, whereas in March–April 1995 only minor amounts of harmonic tremor were recorded (Fig. 2d).

A dramatic decrease in the total number of type B earthquakes (range 511–2192) occurred in February 1996 (Fig. 2e) and continued through December 1997. This change coincided with the apparent migration of the locus of fumarolic activity from beneath the lake to the adjacent composite pyroclastic cone (Fig. 1).

Plume height estimates come from field observations that were calibrated with geodetic equipment. The highest plumes were observed during the period of enhanced volcanic activity from April to September 1994. Plume heights increased steadily from 80 to 1500 m suggesting increases in the amount of energy and gas being released by the volcano (Fig. 5a). On 25 and 30 April 1994, two phreatic eruptions vented grey to clear coloured ash containing old lake-floor sediments that reached 1.6 km south and southwest of the lake. On 2 June, a phreatic eruption column 1.2 km in elevation, vented dry steam and non-juvenile ash up to 1.6 km downwind from the lake. Thirteen moderate size phreatic eruptions occurred between 24–31 July and 4 August 1994. The largest eruption occurred on 31 July and non-juvenile ash was distributed up to 12 km southwest of the summit. Significant increases in the number of type A and B events were recorded prior to and during these eruptions. After the lake reformed in September 1994, the height of the steam plume was greatly reduced (e.g. 80 m, Fig. 5a). Similar periods of elevated plume height were observed during the dry season of 1993 (plume heights upwards of 500 m) and from February 1996 to December 1997, when the locus of most fumarolic activity continued to shift from Laguna Caliente to the composite pyroclastic cone south of the lake. During 1997 only small changes in plume height were recorded.

5. Trends in the chemistry of Laguna Caliente with volcanic activity

Concentrations of chloride and sulfate in Laguna Caliente ranged between 2630 and 85,600 ppm and between 4640 and 91,000 ppm, respectively, for the period of 1993–1997. Lake-water pH ranged from near zero to 1.85 (Table 1, Fig. 3b–d). Sulfate and chloride concentrations were higher, and lake-water pH values lower in 1993–1994, relative to the period 1995–1997 (Martínez et al., 1997). Maximum sulfate and chloride concentrations were recorded near the end of the 1993 dry season. After the dry season of 1994, concentrations of chloride and sulfate declined in a more or less steady manner until mid-1997 when slight increases took place (Fig. 3b,c).

During the dry season of 1993, the lake ranged from small pools to a lake with a volume of nearly $4.7 \times 10^4\ m^3$ (Fig. 2b). Later that year, during the rainy season (May–December,1993), a minor increase in the lake-water pH was observed (~0.3) possibly caused by dilution associated with refilling of the lake by rainwater (Figs. 2a,b, 3d). From April 1993 to March 1994, the sulfate/chloride concentration ratio of the lake water increased, possibly in response to a decrease in lake water chloride due to volatilisation of HCl (Rowe et al., 1992a).

A sharp increase in acidity, sulfate and chloride is noted in February–March 1994, prior to the disappearance of the lake and before the onset of the period of enhanced volcanic activity (Figs. 3b–d). Despite this, no significant changes in lake temperature (which remained near 60°C) were observed at this time. In April 1994, the lake volume was reduced to scattered small mud pools of highly variable temperature and composition (Smithsonian Institution, 1994a). From March to July 1994, an increase in type B seismicity was recorded at POA2 station suggesting an increased level of volcanic activity beneath the crater lake. Type A seismicity and the number of harmonic tremor hours also increased, but only after the lake had disappeared in April 1994. The numerous low-frequency events are believed to reflect shallow seismic signatures of degassing from the magma, whereas the origin of the tremors may relate to magma movement (McNutt and Harlow, 1983; Ferruci, 1995). Elevated seismic activity, low pH and high concentrations of chloride and sulfate strongly suggest vigorous degassing of subaqueous fumaroles into the lake at this time. The cause of the intense fumarolic discharge and associated increase in seismic activity beneath the active crater could be either a hydrofracturing event or the ascent of a small volume of fresh magma. Support for the above hypotheses is provided by remote temperature measurements of the most intense fumarole vents exposed after the lake dried up completely in April 1994. Fumaroles on the dry lake bottom registered

Table 1
Analytical results and physical parameters of Laguna Caliente, Volcán Poás

Date of sampling	Temperature (°C)	pH (23°C)	Cl^- (mg l^{-1})	SO_4^{2-} (mg l^{-1})	Lake volume (m^3)	Lake depth (m)
9 Jan 93	65	0[a]	49,100	54,000	4.7×10^4	2.5
6 Feb 93	70	0	56,100	58,000	2.8×10^4	1.5
20 Feb 93	60	0	75,900	84,000	–	–
4-Mar 93	60	0	75,500	65,000	1.9×10^4	1
14 Apr 93	60	0	61,200	55,000	1.9×10^4	1
16 Apr 93	60	0	24,500	47,000	–	–
14 May 93	63	0	85,600	91,000	7.5×10^3	0.4
11 Jun 93	65	0.30	36,400	35,700	1.9×10^4	1
9 Sep 93	64	0.35	29,600	50,400	6.5×10^4	3.5
22 Oct 93	60	0.30	27,600	45,900	7.1×10^4	3.8
10 Dec 93	60	0.30	25,300	40,700	7.5×10^4	4
4 Feb 94	60	0	32,800	62,100	7.7×10^4	4.1
12 Mar 94	55	0	56,500	83,100	2.8×10^4	1.5
11 May 94	65	0	12,700	19,000	9.0×10^3	0.5
19 May 94	65	0	17,700	17,500	–	–
4 Jun 94	70	1.00	25,500	19,400	7.5×10^3	0.4
10 Jun 94	65	0.80	24,000	9630	–	–
8 Jul 94	65	0.70	16,500	24,900	3.7×10^3	0.2
30 Aug 94	60	0.54	10,100	19,200	2.8×10^4	1.5
9 Sep 94	65	0.60	15,600	15,300	9.3×10^4	5
23 Sep 94	65	0.30	24,000	27,000	–	–
21 Oct 94	60	0.14	8470	17,000	–	–
15 Nov 94	55	0.38	7640	11,000	2.8×10^5	12.1
6 Jan 95	50	0.22	10,200	16,000	–	–
3 Feb 95	47	0.18	10,100	16,600	4.0×10^5	16.3
10 Mar 95	42	0.20	7780	20,400	–	–
28 Apr 95	41	0.35	8000	21,900	–	–
19 May 95	43	0.46	5240	10,800	4.2×10^5	16.9
2 Jun 95	39	0.35	5180	9970	4.3×10^5	17.3
30 Jun 95	39	1.30	4740	9510	–	–
26 Aug 95	36	1.15	5010	9510	–	–
22 Sep 95	34	1.15	4390	8870	–	–
20 Oct 95	30	1.25	3800	6220	7.4×10^5	25.5
17 Nov 95	26	1.20	3710	7050	–	–
15 Dec 95	30	1.30	3632	6860	7.9×10^5	26.5
5 Jan 96	30	1.35	3590	9060	–	–
26 Jan 96	30	1.45	3370	7310	–	–
30 Jan 96	26	1.45	3370	6680	–	–
23 Feb 96	27	1.55	2630	4480	–	–
22 Mar 96	30	1.50	3370	6270	9.9×10^5	30.6
12 Apr 96	34	1.85	4230	5970	–	–
26 Apr 96	36	1.50	3910	5290	–	–
10 May 96	36	1.45	4010	5180	–	–
18 May 96	39	1.45	4280	5410	–	–
31 May 96	42	1.30	4330	5060	–	–
14 Jun 96	45	1.35	4390	7000	–	–
24 Jul 96	36	1.80	4460	7520	–	–
8 Aug 96	34	1.45	4510	6970	1.4×10^6	38.5
30 Aug 96	36	1.50	4370	7020	–	–
27 Sep 96	40	1.65	4320	6780	1.5×10^6	38.7
5 Nov 96	35	1.50	5350	7170	–	–
28 Nov 96	31	1.55	5110	6790	–	–

Table 1 (*continued*)

Date of sampling	Temperature (°C)	pH (23°C)	Cl^- (mg l^{-1})	SO_4^{2-} (mg l^{-1})	Lake volume (m^3)	Lake depth (m)
18 Dec 96	29	1.50	3650	4870	1.5×10^6	39.3
7 Jan 97	32	1.40	5750	6880	1.5×10^6	40.4
4 Feb 97	31	1.40	3850	5110	–	–
3 Mar 97	29	1.55	3260	4410	1.5×10^6	40.5
4 Apr 97	29	1.40	4330	4870	–	–
17 Apr 97	28	1.30	4230	4640	–	–
21 Apr 97	25	1.30	4570	4990	–	–
14 May 97	29	1.45	4420	4640	–	–
4 Jun 97	35	1.50	4280	4750	1.6×10^6	41.3
2 Jul 97	32	1.50	4620	4870	–	–
28 Jul 97	31	1.60	4735	5120	–	–
5 Sep 97	33	1.03	5290	4640	1.7×10^6	42.6
5 Sep 97	33	1.35	4330	4060	–	–
19 Sep 97	35	1.45	5750	5320	–	–
3 Oct 97	35	1.41	7580	6340	–	–
17 Oct 97	35	1.30	5980	6220	–	–
17 Oct 97	34.5	1.30	6520	7840	–	–
4 Nov 97	34	1.40	7800	6460	–	–
25 Nov 97	35	1.25	7660	6850	–	–
28 Nov 97	35	1.35	6900	6400	–	–

[a] Note: the analogic pH-meter indicated pH zero (it means that the pH was below or near zero).

515°C with an optical pyrometer on 21 July 1994 when plume heights were 1500 m (Fig. 5a).

Lake temperature, acidity, sulfate and chloride concentrations continued to decrease steadily with some minor fluctuations through mid-1995 after the lake reformed and eruptive activity waned in August–September 1994. By mid-1995, declines in the concentration of chloride had leveled out whereas sulfate concentrations continued to decline steadily through early 1996 (Fig. 3b,c). Although some variation in the sulfate/chloride concentration ratio is observed after the lake reforms in September 1994, the rather narrow range of sulfate/chloride values suggests that the observed declines in sulfate and chloride largely reflect a dilution trend caused by the addition of meteoric water that refilled the lake (Fig. 3a–c, 2b).

From October 1995 to January 1996, a new increase in type A, type B and tremor seismicity was recorded at Poás volcano. The number of type A events and the amount of harmonic tremor hours were slightly higher than those recorded during period of enhanced activity in mid-1994 (Fig. 2d). Despite this period of enhanced seismicity, lake temperature declined further reaching the minimum recorded value for the period 1993–1997 (25°C) and lake volume continued to increase (Fig. 2b). Elevated levels of seismic activity suggest changes in the subsurface hydrothermal–magmatic system that were not reflected by changes in the crater lake. Instead, field observations made during December 1995 indicate an increase in the size and relative intensity of fumarolic discharge from the pyroclastic cone including renewed deposition of native sulfur at several of the newly formed fumaroles. Although not as impressive as the increase in fumarolic activity recorded after the intense seismic swarm of July 1980, these observations suggest a similar migration of fumarolic activity from beneath the crater lake back to the pyroclastic cone. The migration of most fumaroles to the pyroclastic cone near the end of 1995 coincides well with a gradual reduction in lake acidity and the steady increase in lake volume that was recorded in 1996 (Smithsonian Institution, 1996b).

From March 1996 to December 1997, there were several months where more than 10 type A seismic events were recorded. Periods in which notable increases in the number of type A events were recorded include August–September 1996 and January–February 1997 when more than 50 events were recorded each month. However, periods of harmonic tremor were less common, with minor periods of harmonic tremor recorded over the period February–June 1996, October 1996, and following a year of no harmonic tremor, again in November–December 1997 (Fig. 2d). The peaks of type A seismicity and periods of harmonic tremor are not related to any significant changes in lake temperature or chemistry, but instead appear to coincide with new fumarole opening events within the main crater of Poás or with areal expansion of the pre-existent fumaroles (Fig. 1).

Finally, despite the overall dilutional trend that accompanied the refilling of the lake, estimates of the total mass of chloride and sulfate in the crater lake show overall increases in the amount of chloride and sulfate stored in the lake between 1994 and 1997. This indicates that subaqueous fumaroles continued to discharge magmatic gas-bearing steam into the crater lake. The trend for sulfate in the lake shows a general increase through mid-1996 and then it levels off and remains nearly constant through November 1997 (Fig. 4).

6. Trends in the chemistry of rain water with volcanic activity

The distribution of acid rain is largely controlled by the interaction of prevailing winds, that blow southwest across the summit area, with the morphology of the area near and downwind of the active crater. The chemistry of rainwater samples collected at the Cerro Pelón site, 2.4 km downwind of the active crater, is quite variable (Fig. 5). Composite monthly samples of both wet and dry acid deposition collected between 1993 and 1997 had pH values between 2.9 and 5.8. Sulfate and chloride concentrations in the rainwater samples range from 0.8 to 376 ppm sulfate and 0.6 to 85 ppm chloride. These values are similar to those reported by Rowe et al. (1995) for acid rain samples collected during the period 1988–1990 at various locations on the southwest flank of Poás (1.7–46 ppm sulfate; 3.1–49 ppm chloride).

Higher chloride concentrations were recorded in January–June 1993 (85 ppm), in March–August 1994 (81 ppm) and in April–July 1996 (41 ppm). The first two periods of high chloride concentration in acid rain occur within the dry season (Fig. 2a) and correlate with periods of low lake volume and elevated lake temperature, whereas the second and third periods are correlated with periods of enhanced type A and harmonic tremor activity. The latter period in April–July 1996 also was correlated with a short-lived six-degree increase in lake temperature (Fig. 2c). High chloride concentrations in acid rain waters may reflect enhanced volatilisation of HCl from the crater lake surface caused by increases in lake temperature and acidity. Such episodes should be reflected by declines in the sulfate/chloride ratios of

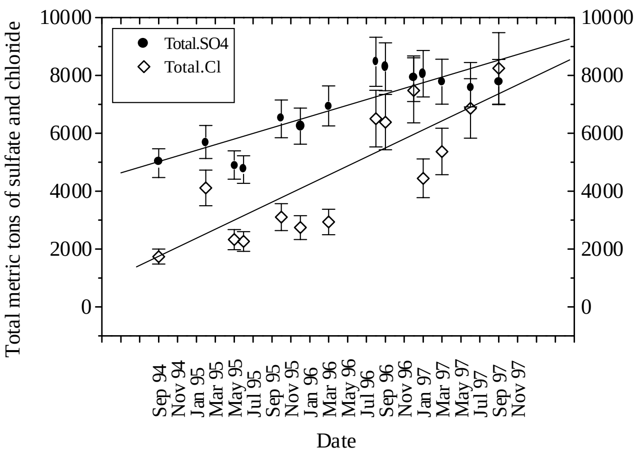

Fig. 4. Temporal variation of the total mass of chloride and sulfate as a function of the crater lake volume (1994–1997).

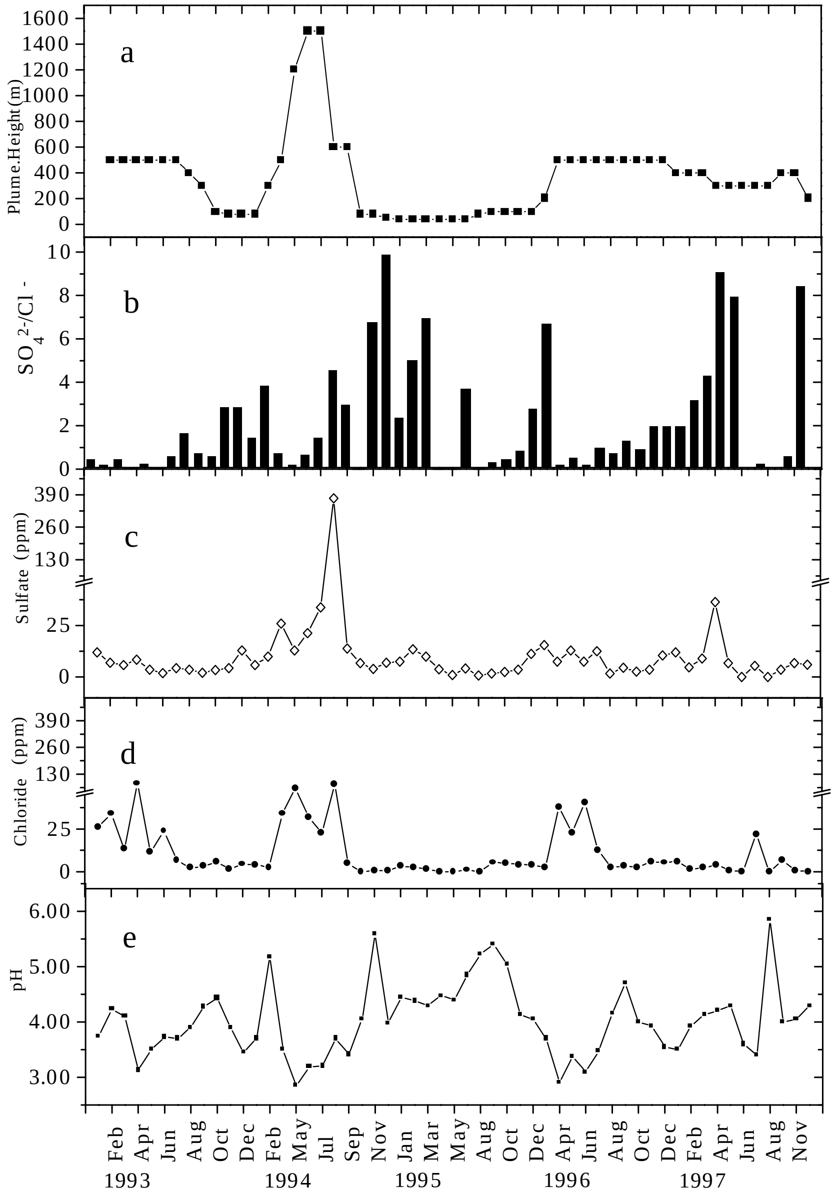

Fig. 5. Monthly variation of rainwater chemical parameters from Cerro Pelón (2.4 km southwest of Laguna Caliente) and maximum plume heights from Poás volcano eruptive plumes, between 1993–1997 including: (a) maximum measured plume heights; (b) SO_4^{2-}/Cl^- concentration ratio; (c) sulfate concentration; (d) chloride concentration; and (e) pH.

acid-rain samples (Fig. 5b) as observed prior to the first disappearance of the lake in early 1989 (Rowe et al., 1992a). Higher sulfate concentrations in acid rain were recorded twice during the period under consideration (March–September 1994 and April 1997). Elevated sulfate concentrations appear to be related to an increase in the release of sulfate-rich particles during steam eruptions or by the release of hydrogen sulfide gas from new, low-temperature fumaroles that reappeared on the pyroclastic cone in late 1995.

The area affected by volcanic emissions had elliptical shape with its major axis oriented to the southwest of the summit area (Fig. 6). In January 1994, the approximate area affected was a 3-km ellipse with a total area approaching 4 km^2. In May 1994, the area affected had increased to ca. 50 km^2 (ellipse axis: 12 km) and by July–August 1994, the area reached an estimated maximum of 74 km^2 (ellipse axis: 15 km, Fig. 6). On basis of the estimates made by the Costa Rican Agricultural Extension Agency, losses to crops caused by the period of enhanced acid deposition in 1994 approached 1.5 million dollars (N. Kopper, Costa Rican Agricultural Extension Agency, pers. commun., 1995). About two thirds of the economic loss came from lower productivity in coffee plantations. Other areas affected by the acid emissions included timber, crops, machinery, grazing land, native vegetation (Sandoval, 1996), livestock, housing and human and animal health (Baxter et al., 1997). Health complaints included nausea, coughing and irritated throat, eyes and skin (Smithsonian Institution, 1994a,b).

7. Conclusions

The classification scheme for volcanic lakes proposed by Pasternack and Varekamp (1997) divides volcanic lakes in five categories based on physical and chemical properties of the lake. During the period 1993–1997, three of their categories can be used to describe the evolution of Laguna Caliente. Using the sum of chloride and sulfate as a proxy for TDS, the general physico-chemical evolution of Poás crater

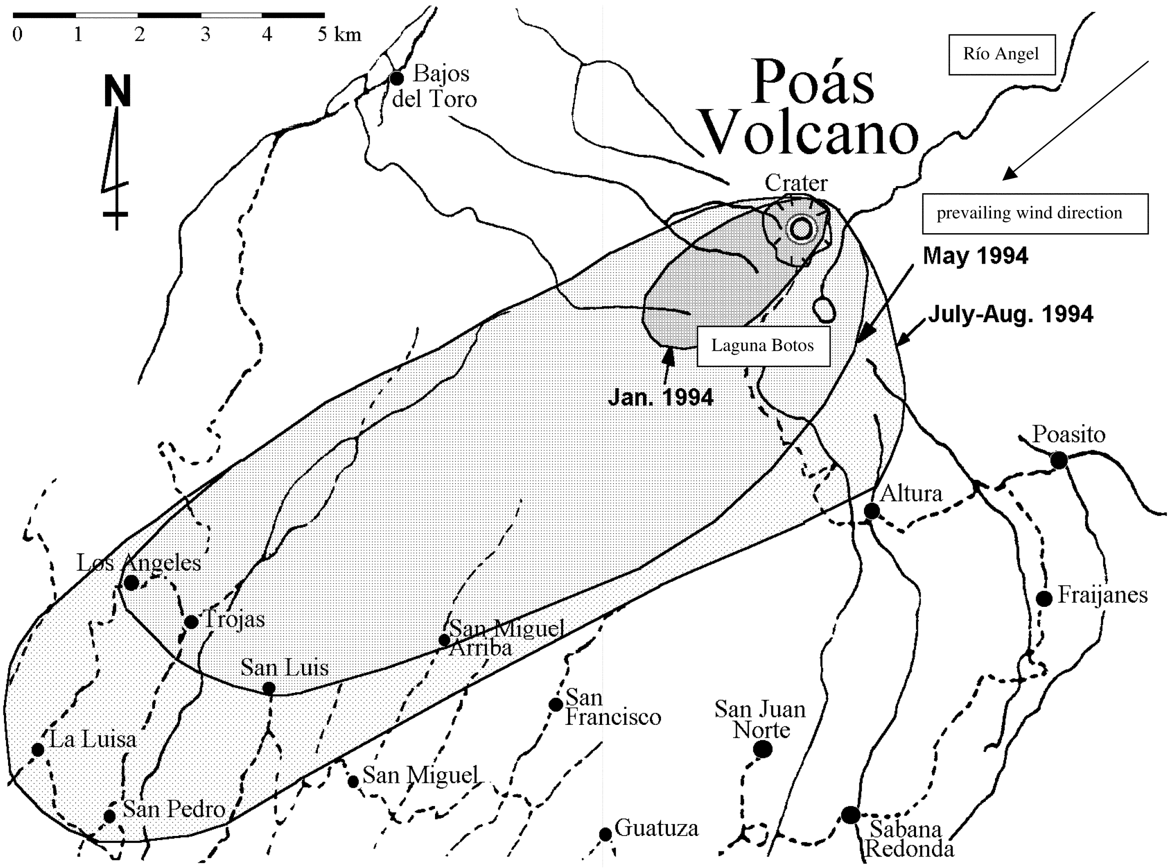

Fig. 6. Map of Poás volcano showing areas affected by the volcanic emissions at three different dates: January 1994, May 1994 and July–August 1994, right after the phreatic eruptions occurred in late July and early August 1994. The prevailing wind direction is shown on the figure (from northeast to southwest).

lake can be described as follows: (1) a period of peak activity from January 1993 to approximately February 1995 when lake pH was consistently near zero, lake temperature usually exceeded 45°C, and the combined concentration of chloride and sulfate ranged from 17.7 to 1.8%; (2) a short transitional period from March 1995 to September 1995 corresponding to the high activity period when the lake typically had pH values between 0.3 and 1.0, temperatures between 35 and 45°C, and chloride plus sulfate concentrations of 1.3–2.8%; and (3) a period of medium activity from October 1995 to December 1997 during which lake pH was between 1.0 and 2.0, lake temperature was generally less than 35°C and the combined concentration of chloride and sulfate was generally less than 1% (10,000 mg l^{-1}).

The geochemical properties of Laguna Caliente, as well as variations in its temperature, volume and depth, reflect both climatic effects and interactions with a shallow subsurface magma body and associated magmatic–hydrothermal system. Therefore, changes in parameters normally associated with volcanic activity such as increased seismicity, plume height or fumarole temperature will tend to be related to changes in crater-lake chemistry, particularly for species derived from magmatic gases (e.g. acidity, chloride and sulfate). The relation between these parameters will be more evident when fumarolic discharge from the underlying magmatic–hydrothermal system is focused beneath the lake, as was the case between 1993 and January 1996.

During April–August 1994, plume heights (1500 m) and fumarole temperatures (515°C) recorded on the lake bottom increased dramatically suggesting a large increase in the flux of heat from the shallow magma body. Between September 1995 and January 1996 renewed magmatic–hydrothermal activity opened a new path for the ascending gases to the surface as the fumaroles beneath the lake became gradually sealed after September 1994. As a result, fumarolic activity appeared to migrate from beneath the crater lake to the pyroclastic cone on the south rim of the crater lake.

After the fumarolic activity migrated to the pyroclastic cone, intensive fumarolic outgassing started to interact directly with the atmosphere decreasing the direct contribution of chemical species to the crater lake. Under the new conditions, the concentration of anions in the lake and its physical parameters (i.e. temperature) did not respond directly to changes in seismic activity. Type B events which are normally considered indicators of hydrothermal activity decreased dramatically suggesting smaller interaction of ascending gases with the volcano's hydrothermal system.

In general terms, the physico-chemical properties of Laguna Caliente evolved from those characteristic of a hot acidic hyperbrine to those of an acid-saline brine between 1993–1997. The hot acid hyperbrine corresponds to the period in which the focus of subsurface magmatic–hydrothermal activity was beneath the crater lake whereas the acid-saline brine corresponds to the period in which the activity migrated back to the pyroclastic cone (i.e. after January, 1996). Migration of activity from one vent to the other has been a common feature at Poás and the return of the crater lake to a more quiescent state may mark the end of the period of lake instability that began in mid-1986 (Brown et al., 1991; Rowe et al., 1992a,b).

Decreases in the sulfate/chloride ratio of acid rain were caused by volatilisation of chloride from the lake as temperature, acidity and anions concentration increased as the volcano activity increased. However, the ratio observed in acid deposition samples is affected by the efficiency of HCl absorption by rainwater and also by the form in which sulfur species are emitted by the volcano. The observations presented here suggest that the crater lake has a significant role in determining the type and intensity of acid deposition, with periods of enhanced acid deposition and increased economic damage occurring when the lake declines or disappears.

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References

Badrudin, M., 1994. Kelut volcano monitoring: Hazards, mitigation and changes in water chemistry prior to the eruption. Geochem. J. 28, 233–241.

Barquero, J., Fernández, E., 1988. Estado de los volcanes, Enero-Diciembre 1987. Bol. Vulcanol. 19, 5.

Barquero, J., Fernández, E., 1990. Erupciones de gases y sus consecuencias en el Volcán Poás Costa Rica. Bol. Vulcanol. 21, 13–18.

Barquero, J., Malavassi, E., 1981. Estado de los volcanes, diciembre 1980-febrero 1981. Bol. Vulcanol. 10, 6–7.

Barquero, J., Malavassi, E., 1981. Estado de los volcanes, marzo-junio 1980. Bol. Vulcanol. 11, 3–4.

Barquero, J., Malavassi, E., 1982. Estado de los volcanes, julio 1981-marzo 1982. Bol. Vulcanol. 12, 1.

Barquero, J., Malavassi, E., 1983. Estado de los volcanes, mayo 1982-abril 1983. Bol. Vulcanol. 13, 3.

Baxter, P., Alfaro, M.R., Moreno, N., Solís, P., 1997. Poás volcano acid precipitation assessment project. Final report no. 2-07-97. Universidad Nacional, Costa Rica, p. 25.

Bennett, F., Raccichini, S., 1978. Nuevos aspectos de las erupciones del Volcán Poás. Rev. Geogr. Am. Centr. 5,6, 37–54.

Bennett, F., Raccichini, S., 1978. Subaqueous sulphur lake in volcán Poás. Nature 271, 342–344.

Bennett, F.D., 1979. Fumarolas y pozos subacuáticos de azufre en el volcán Poás Costa Rica. Rev. Geogr. Am. Centr. 11,12, 125–130.

Boza, M.A., Mendoza, R., 1981. The national parks of Costa Rica. Industrias Gráficas Alui. S.A., Madrid, p. 310.

Brantley, S.L., Borgia, A., Rowe, G., Fernández, J.F., Reynolds, J.R., 1987. Poás volcano crater lake acts as a condenser for acid metal-rich brine. Nature 330, 470–472.

Brown, G., Rymer, H., Dowden, J., Kapadia, P., Stevenson, D., Barquero, J., Morales, L.D., 1989. Energy budget analysis for Poás Crater lake: implications for predicting volcanic activity. Nature 339, 370–373.

Brown, G.C., Rymer, H., Stevenson, D.S., 1991. Volcano monitoring by microgravity and energy budget analysis. J. Geol. Soc. (London) 148, 585–593.

Calvert, A.S., Calvert, P.P., 1917. A year of Costa Rican natural history. Mac Millan, New York, p. 577 chap. XVII.

Casertano, L., Borgia, A., Cigolini, C., Morales, L.D., Gómez, M., Fernández, J.F., 1987. An integrated dynamic model for the volcanic activity at Poás volcano, Costa Rica. Bull. Volcanol. 49, 588–598.

Fernández, M., 1990. Actividad del volcán Poás, Costa Rica: Análisis sísmico durante el período 1980–1989. Tesis de Licenciatura, Escuela Centroamericana de Geología, Universidad de Costa Rica, América Central.

Fernández, E., Barquero, J., Barboza, V., Vander Laat, R., Marino, T., Obaldía, F., 1994. Estado de los Volcanes, 1992. Bol. Vulcanol. 23, 5–11 OVSICORI-UNA: Costa Rica.

Ferrucci, F., 1995. In: McGuire, W.J., Kilburn, C., Murray, J.B. (Eds.), Seismic Monitoring at Active Volcanoes. UCL, London, pp. 60–92.

Francis, P.W., Thorpe, R.S., Brown, G.C., Glasscock, J., 1980. Pyroclastic sulphur eruption at Poás volcano Costa Rica. Nature 283, 754–756.

Krushensky, R.D., Escalante, G., 1967. Activity of Irazú and Poás volcanoes Costa Rica, November 1964–July 1965. Bull. Volcanol. 31, 75–84.

Liao, A., 1997. Climatología de las áreas circunvecinas al Volcán Poás. Technical report, Instituto Meteorológico Nacional de Costa Rica (IMN), p. 39.

Malavassi, E., Barquero, J., 1982. Excursión al Volcán Poás. Proceedings of the First US Costa Rica Joint Seminar in Volcanology. Bol. Vulcanol. 14, 119–131 OVSICORIUNA: Costa Rica.

Malavassi, E., Barquero, J., Fernández, E., Barboza, V., Van der Laat, R., Marino, T., De Obaldía, F., 1993. Excursión al Volcán Poás. IV. Taller Regional Sobre Metodologías de Vigilancia Volcánica con Enfasis en Gases Volcánicos. OVSICORI-UNA: Costa Rica, pp. 1–26.

Martínez, M., Sandoval, L., Valdés, J., Valverde, J., Fernández, E., Duarte, E., Barquero, J., Malavassi, E., 1997. Changes in the chemical characteristics of Poás volcano's crater lake between 1993 and 1996, Costa Rica. Newsletter IAVCEI Commission on Volcanic Lakes, UK. no. 10 pp. 22–27

McNutt, S.R., Harlow, D.H., 1983. Seismicity at Fuego Pacaya, Izalco and San Cristóbal volcanoes, Central America. Bull. Volcanol. 46, 283–297.

Minakami, T., 1969. Earthquakes originating from volcanoes. Atti. XVIII, Conv. Ass. Geof. Ital., Napoli.

Oppenheimer, C., Stevenson, D., 1989. Liquid sulfur lakes at Poás Volcano. Nature 342, 790–793.

Pasternack, G., Varekamp, J., 1997. Volcanic lake systematics. I. Physical constraints. Bull. Volcanol. 58, 534–535.

Prosser, J.T., 1985. Geology and medium-term temporal magmatic variation fund at the summit region of Poas volcano, Costa Rica. Bol. Vulcanol. 15, 21–39.

Prosser, J.T., Carr, M.J., 1987. Poás volcano, Costa Rica: geology of the summit region and spatial and temporal variations among the most recent lavas. J. Volcanol. Geotherm. Res. 33, 131–146.

Protti, M., McNally, K., Pacheco, J., González, V., Montero, C., Segura, J., Brenes, J., Barboza, V., Malavassi, E., 1995. The March 25, 1990 ($M_w = 7.0$, $M_L = 6.8$), earthquake at the entrance of the Nicoya Gulf, Costa Rica: its prior activity, foreshocks, aftershocks, and triggered seismicity. J. Geophys. Res 100 (20), 345–358.

Raccichini, S., Bennett, F.D., 1977. Nuevos aspectos de las erupciones del volcán Poás. Rev. Geogr. Am. Centr. 5-6, 37–53.

Rowe, G.L., 1994. Oxygen, hydrogen, and sulfur isotope systematics

of the Crater Lake system of Poás Volcano, Costa Rica. Geochem. J. 28, 264–275.
Rowe, G.L., Ohsawa, S., Takano, B., Brantley, S.L., Fernández, J.F., Barquero, J., 1992. Using Crater Lake chemistry to predict volcanic activity at Poás Volcano, Costa Rica. Bull. Volcanol. 54, 494–503.
Rowe, G.L., Brantley, S.L., Fernández, M., Fernández, J.F., Borgia, A., Barquero, J., 1992. Fluidvolcano interaction in an active stratovolcano: the Crater Lake system of Poás Volcano, Costa Rica. J. Volcanol. Geother. Res. 49, 2351.
Rowe, G.L., Brantley, S.L., Fernández, J.F., Borgia, A., 1995. The chemical and hydrologic structure of Poás volcano, Costa Rica. J. Volcanol. Geotherm. Res. 64, 233–267.
Rymer, H., Brown, G.C., 1989. Gravity changes as a precursor to volcanic eruption at Poás volcano, Costa Rica. Nature 342, 902–905.
Rymer, H., Cassidy, J., Locke, C., Barboza, V., Barquero, J., Brenes, J., Van der Laat, R., 2000. Geophysical studies of the recent 15-year eruptive cycle at Poás volcano, Costa Rica. J. Volcanol. Geotherm. Res. 97 (1–4), 425–442.
Sandoval, L., 1996. Efecto de las emisiones volcánicas sobre la vegetación del Parque Nacional Volcán Poás. Tesis de licenciatura, Universidad Nacional: Heredia, Costa Rica, p. 107.
Smithsonian Institution, 1989. Bull. Global Volcanism Network, Poás Volcano 14 (4), 7–10.
Smithsonian Institution, 1990. Bull. Global Volcanism Network, Poás Volcano 15 (4), 6–9.
Smithsonian Institution, 1991. Bull. Global Volcanism Network, Poás Volcano 16, 1–12.
Smithsonian Institution, 1992. Bull. Global Volcanism Network, Poás Volcano 17, 1–12.
Smithsonian Institution, 1993. Bull. Global Volcanism Network, Poás Volcano 18 (2), 1–12.
Smithsonian Institution, 1994a. Bull. Global Volcanism Network, Poás Volcano 19 (5), 12–13.
Smithsonian Institution, 1994b. Bull. Global Volcanism Network, Poás Volcano 19 (4), 4.
Smithsonian Institution, 1996a. Bull. Global Volcanism Network, Poás Volcano 21 (3), 5.
Smithsonian Institution, 1996b. Bull. Global Volcanism Network, Poás Volcano 21 (5), 10.
Takano, B., 1987. Correlation of volcanic activity with sulfur oxyanion speciation in a crater lake. Science 235, 1545–1712.
Takano, B., Watanuki, K., 1990. Monitoring of volcanic eruptions at Yugama Crater Lake by aqueous sulfur oxyanions. J. Volcanol. Geotherm. Res. 40, 71–87.
Takano, B., Saitoh, H., Takano, E., 1994. Geochemical implications of subaqueous molten sulfur at Yugama Crater Lake, Kusatsu–Shirane volcano, Japan. Geochem. J. 28, 199–216.
Takano, B., Ohsawa, S., Glover, R.B., 1994. Surveillance of Ruapehu crater lake, New Zealand, by aqueous polythionates. J. Volcanol. Geotherm. Res. 60, 29–57.
Vargas, C.A., 1979. Antología: El volcán Poás. Universidad Estatal a Distancia, San José, Costa Rica.