Behaviour of Polythionates in the Acid Lake of Poás Volcano: Insights into Changes in the Magmatic-Hydrothermal Regime and Subaqueous Input of Volatiles

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Abstract

In this chapter, we document an extensive record of concentrations and speciation of polythionates (PTs: $S_4O_6^{2-}$, $S_5O_6^{2-}$, and $S_6O_6^{2-}$), which form in the warm (21–60 °C) and hyper-acidic (pH < 1.8) waters of the crater lake of Poás volcano (Costa Rica) through interaction with gaseous SO_2 and H_2S of magmatic origin. Our data set, together with earlier published results, covers the period 1980–2006 during which lake properties and behavior were marked by significant variations. Distinct stages of activity can be defined when combining PT distributions with geochemical, geophysical and field observations. Between 1985 and mid-1987, when fumarolic outgassing was centered on-shore, the total concentration of PTs in the lake was consistently high (up to 4,200 mg/kg). Mid-1987 was the start of a 7-year period of vigorous fumarolic activity with intermittent phreatic eruptions from the lake, which then dried out. Concentrations of PTs remained below or close to detection limits throughout this period. After mid-1994, when a new lake formed and fumarolic outgassing shifted to the dome, the total PT concentrations returned to relatively stable intermediate levels (up to 2,800 mg/kg) marking more quiescent conditions. Since early 1995, numerous weak fumarole vents started, opening up at several other locations in the crater area. During short intervals (November 2001–May 2002 and October 2003–March 2005), PTs virtually disappeared. After April 2005, PTs re-appeared in large amounts (up to more than 3,000 mg/kg) until February 2006, one month before the onset of the March 2006–2017 cycle of phreatic eruptions, when concentrations dropped and remained below 100 mg/kg. The observed behavior of PTs records changes in the input and SO_2/H_2S ratios of subaqueous fumaroles. The prevailing distribution of PTs is $S_4O_6^{2-} > S_5O_6^{2-} > S_6O_6^{2-}$, which is common for periods when total PT concentrations and SO_2/H_2S

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ratios of the gas influx into the lake are relatively high. PTs are virtually absent as a consequence of thermal or sulphitolytic breakdown during periods of strong fumarolic outgassing in response to shallow intrusion of fresh magma or fracturing of the solid envelope around a pre-existing body of cooling magma. They are also low in abundance or undetected during quiescent periods when subaqueous fumarolic output is weak and has low SO_2/H_2S ratios, resulting in a concentration sequence $S_5O_6^{2-} > S_4O_6^{2-} > S_6O_6^{2-}$. The onset of phreatic eruptions are preceded by an increase in PT concentrations, accompanied by a change in the dominance from penta- to tetrathionate, and followed by a sharp drop in total PT content, up to several months before. Periods of phreatic eruptive activity that started in 1987 and 2006 followed these PT signals of increased input of sulfur-rich gas, in both cases possibly in response to shallow emplacement of fresh magma or hydrofracturing.

Keywords

Polythionates · Sulphur chemistry · Acid volcanic lakes · Magmatic volatiles · Magmatic-hydrothermal system · Volcano monitoring · Volcanic unrest

1 Introductory Remarks

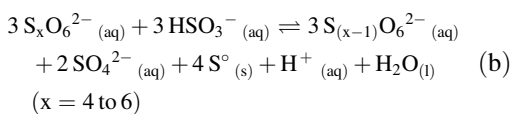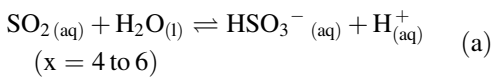## 1.1 Polythionates: Research and Discovery in Waters of Volcanic Origin

A variety of chemical constituents of volcanic lakes and associated fluids is classically employed to monitor volcanic activity, assess the flow rate and nature of volcanic gases expelled from cooling magmas, and study water-gas-rock interactions in shallow magmatic-hydrothermal systems (e.g. Giggenbach 1974; Sigurdsson 1977; Casadevall et al. 1984a; Rowe et al. 1992a, b; Christenson and Wood 1993; Takano et al. 1994a, b; Delmelle and Bernard 1994; Delmelle 1995; Pasternack and Varekamp 1994, 1997; Armienta et al. 2000; Christenson 2000; Delmelle and

Bernard 2000; Delmelle et al. 2000; Martínez et al. 2000; Xu et al. 2000; Sriwana et al. 2000; Varekamp et al. 2001; Tassi et al. 2009; Stimac et al. 2003; Bernard et al. 2004; Takano et al. 2004, 2008; Ohba et al. 2008; Rouwet et al. 2014). Among the more exotic geochemical parameters with monitoring potential are the natural oligomeric sulfur compounds, known as polythionates (PTs), which have the general formula $(O_3SS_nSO_3)^{2-}$, where "n = 2" in tetrathionate (Steudel and Holdt 1986; Shriver and Atkins 1999). They are named according to the total number of sulfur atoms: trithionate ($S_3O_6^{2-}$), tetrathionate ($S_4O_6^{2-}$), pentathionate ($S_5O_6^{2-}$), etc. Trithionate, the shortest PT, will decompose if exposed to acid but tetrathionate, and higher polythionates, are stabilized by acid conditions. Trithionate in low pH < 1 solutions is formed by rearrangement reactions of tetrathionate but it is rapidly oxidized converting tetrathionate to sulfate. Thus, trithionate is not considered in this chapter because it decomposes in acid conditions whereas tetrathionate and higher polythionates are favored by chemical conditions occurring at Laguna Caliente. Oxidation kinetics of PTs studied through Fe^{3+}/O_2 catalysis experiments, indicate that under low pH conditions and excess of Fe^{3+} and O_2, the rate of polythionate oxidation is fast and Fe^{3+} and O_2 somehow control some of the reaction pathways of the oxidation kinetics of the PTs (Druschel et al. 2003).
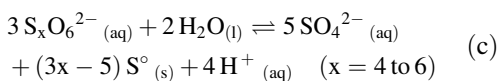
Polythionates were found in waters of volcanic origin for the first time in New Zealand when MacLaurin (1911) discovered pentathionate in the crater lake of White Island Volcano. Day and Allen (1925) reported the presence of pentathionate and possibly that of tetrathionate, and trithionate in the hot springs of Lassen Peak whilst Wilson (1941, 1953, 1959) recognized various PTs in waters from the Black Pool near Rotorua and the Black Geyser at Ketetahi thermal springs. The boiling springs of Yellowstone National Park have also been studied for total PTs and other sulfur species (Xu et al. 2000). However, the research on the complex chemistry of the polythionates started earlier in the 19th century. Dalton in 1808 in his "A New System of Chemical Philosophy" commented on the chemical nature of

the constituents of the liquid, which later came to bear the name Wackenroder (Foss 1960). The three lowest acids were discovered between 1840 and 1846 by Langlois, Fordos and Gelis (Janitzki 1969), and later Debus (1888) from Wackenroder's liquids isolated a salt that analyzed for potassium hexathionate. The Wackenroder's solution is a milky liquid produced by the reaction of SO_2 and H_2S gases in an aqueous solution originating a mixture of colloidal sulfur, precipitated sulfur, sulfur in solution, traces of sulfate, and at least three polythionates (tri-, tetra- and pentathionate) (Koh 1990). Chemists discovered that tetrathionate was the predominant product and that the pentathionic acids in the Wackenroder's solution decompose into sulfur and tetrathionates under alkaline conditions but are more stable in presence of other acids such as H_2SO_4 and HCl (Debus 1888).

Polythionates as well as a variety of sulfur species, including sulfate (mainly as bi-sulfate), bi-sulfite, are transient sulfur compounds formed in acid aqueous environments such as acid volcanic lake systems by reaction between SO_2 and H_2S gases (Takano and Watanuki 1990; Takano et al. 1994b) from subaqueous fumaroles entering the lake at relatively high SO_2/H_2S ratio (Goehring 1952). Polythionates reach maximum concentrations when this ratio is around 0.13, but they are decomposed via sulfitolysis at higher ratios, yielding elemental sulfur and sulfate as main products (Takano et al. 2001) according to:

$$SO_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons HSO_3^-{}_{(aq)} + H^+_{(aq)} \qquad (a)$$
$$(x = 4\,to\,6)$$

$$3\,S_xO_6^{2-}{}_{(aq)} + 3\,HSO_3^-{}_{(aq)} \rightleftharpoons 3\,S_{(x-1)}O_6^{2-}{}_{(aq)}$$
$$+ 2\,SO_4^{2-}{}_{(aq)} + 4\,S^\circ{}_{(s)} + H^+{}_{(aq)} + H_2O_{(l)} \qquad (b)$$
$$(x = 4\,to\,6)$$

Decomposition will also occur as a result of increasing temperature:

$$3\,S_xO_6^{2-}{}_{(aq)} + 2\,H_2O_{(l)} \rightleftharpoons 5\,SO_4^{2-}{}_{(aq)}$$
$$+ (3x - 5)\,S^\circ{}_{(s)} + 4\,H^+{}_{(aq)} \quad (x = 4\,to\,6) \qquad (c)$$

Hence, SO_2-induced or thermal decomposition of PTs will contribute to an (extra) increase in the total sulfate concentration of an acidic crater lake. For example, significant increases in the concentration of sulfate in the Yugama crater lake were accompanied by breakdown of PTs during periods of phreatic activity (Takano and Watanuki 1990). Polythionates as well as other sulfur species can also be produced by the hydrolysis of elemental sulfur, which abounds in the form of molten sulfur at the interface between the bottom of the hyper acid lakes and their underlying hydrothermal systems (Delmelle and Bernard 2015).

Polythionates in acid volcanic lakes may range in abundance from trace or minor amounts to several hundreds or thousands of mg/l. They have been detected in acid volcanic lakes with pH < 3 such as those at Kusatsu-Shirane (Takano 1987; Takano and Watanuki 1990; Takano et al. 2008), Ruapehu (Takano et al. 1994b), Poás (Rowe et al. 1992b), Keli Mutu Tiwu Nua Muri Koohi Fah (Pasternack and Varekamp 1994), Patuha (Sriwana et al. 2000), Kawah Ijen (Delmelle and Bernard 1994; Takano et al. 2004), Santa Ana (Bernard et al. 2004), Maly Semiachik (Takano et al. 1995), El Chichón (Casas et al. 2015), and Rincón de la Vieja (B. Takano and M. Martínez, unpublished data). Despite the reported presence of PTs in a number of volcanic acid lakes and their monitoring potential (see Delmelle and Bernard 2015 for a recent review), a long-term behavior of PT species was only investigated at Kusatsu-Shirane, Ruapehu and Poás acid lakes. The main reason for that is that polythionates are labile sulfur species at pH > 3, sensitive to Eh-pH, ionic strength, temperature, dissolved SO_2 and H_2S and microbial metabolism in the waters of the acid lakes. Nowadays, chemists continue investigating polythionates as testified by a recent method to produce stable non toxic salts of polythionic acids based on the Smolyaninov reaction for its potential application in safe gold leaching instead of cyanation or mercury amalgamation (Smolyaninov et al. 2014). This is a promising approach and we hope these new stable polythionates will soon be available. Thus, separation and quantification of polythionate species could be continued for the benefit of volcano surveillance and research on magmatic fluids worldwide.

1.2 The *Laguna Caliente at* Poás

1.2.1 Summary of Historical Activity

Poás (10° 11′ 26″N–84° 13′ 56″W), one of the most active volcanoes in central Costa Rica where about 60% of the inhabitants of the country live (Fig. 1), has shown persistent fumarolic degassing with large fluctuations, periods of phreatic explosions in its hyperacid lake and rare strombolian to vulcanian eruptions

during at least the last two and a half centuries. The largest historic eruption (vulcanian type) occurred in 1910 when a major steam and ash cloud rose up to ca. 8 km above the summit (Calvert and Calvert 1917). A period of moderate phreatic and phreatomagmatic eruptions occurred between 1952 and 1955, drying out the crater lake and forming a dome, a small lava flow, and a pit crater that hosted an acid lake in the 60s, (Krushensky and Escalante 1967; Bennett and

Fig. 1 Overview of the summit area of Poás and sampling sites. Cross section (**a**) and bathymetric contours (**b**) are from a survey carried out in early 2001 (adapted from Tassi et al. 2009). Black star in diagram B is the location where lake waters were regularly collected
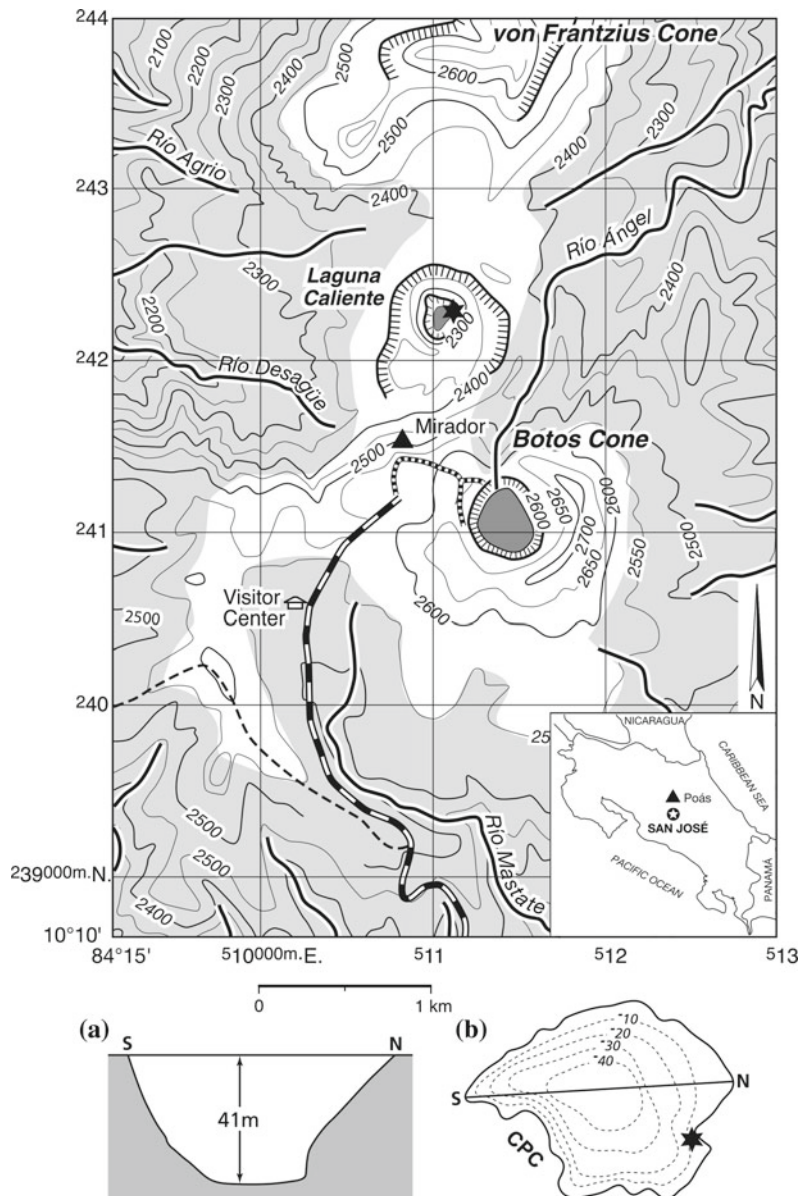
Raccichini 1978a, b). Periods with phreatic explosions from the lake ranging from gas bursts to ejection of gas and vapor columns mixed with sediments, ballistics, and lake water up to several dozens and hundreds of meters high have occurred intermittently since then. The most recent eruptive period with phreatic, strombolian and vulcanian phases with erupted products ranging between basalt-andesitic and andesitic composition (Martínez et al. 2017), occurred between 23 April and late June 2017, preceded by conspicuous geophysical and geochemical changes ca. 1 month in advance: rapid increase in seismic activity, ground deformation (inflation), sharp rise in the magmatic volatile and thermal power output, enrichment of the hyperacid lake in halogens of volatile origin, and remarkable and rapid increase in the lake level and the water table at the bottom of the active crater, despite of absence of rainfall. This eruption triggered small lahars in several of the rivers draining toward the Atlantic slope, destroyed the dome formed in the previous magmatic eruptive period of 1952–1955, and dried out the hyperacid lake (Laguna Caliente) allowing fumaroles enriched in magmatic volatiles and particles to discharge directly into the atmosphere. The overall activity ceased gradually throughout the second half of 2017 and the first half of 2018, and only low temperature fumaroles (92 °C) and boiling mud pools remained a the dried bottom of the crater.

1.2.2 Laguna Caliente and First Polythionate Data

The warm and hyperacid lake of Laguna Caliente, that was stable between mid 1994 and early April 2017, registered temperature, pH and TDS values ranging between 19 °C and 65 °C, below zero and 1.8, and 10^4–10^3 mg/kg, respectively. The lake reached about 300–350 m in diameter and up to 40–50 m deep when at its high level. Sub-aerial fumarolic activity was mainly centered at the dome that was at the southern edge of the lake (Fig. 1) and recently destroyed by the eruptions of April 2017. The dome usually presented low temperature fumaroles (at about boiling point of water at the altitude of the summit: 92 °C) but occasionally it reached up to ca. 900 °C (in 2011)

and around 1000 °C (in 1981 and 2017). Other low temperature fumarole fields have appeared elsewhere within the crater as well (e.g. Vaselli et al. 2003, Chap. 10; Martínez 2008). The intermittent, though frequent, eruptive behavior, and strong temporal variability in lake properties and fumarolic manifestations testify that the Poás volcanic-hydrothermal system is highly dynamic and sensitive to input from magmatic and meteoric sources.

Rowe et al. (1992b) reported the first PT data for Poás's Laguna Caliente, covering the period 1980-early 1990 when the lake evolved from relative quiescence to an interval of high activity (see Martínez 2008 for a summary of the historic activity of Poás). In the early 1980s the authors noticed relatively moderate concentrations of total polythionates with the pentathionate as the predominant species as well as a sharp decrease in PT concentrations three months prior to the recurrence of phreatic eruptions in 1987. They suggested that rapidly changing PT stability and speciation could be a precursor signal of changes in the magmatic-hydrothermal system that affect subaqueous fumarolic input and trigger phreatic activity. Since then, several other periods of eruptions have occurred (phreatic in 2006–2016 and phreatomagmatic to strombolian in the first half of 2017), as well as frequent, sometimes drastic, fluctuations in the physicochemical properties of the crater lake (Martínez et al. 2000; Venzke et al. 2002; OVSICORI open reports; Martínez 2008; Rouwet et al. Chapter "39 Years of Geochemical Monitoring of Laguna Caliente Crater Lake, Poás: Patterns from the Past as Keys for the Future"). This unstable behavior of the volcano provides a unique opportunity to evaluate the response of PTs to marked changes in the input of magmatic volatiles and heat, and to test their value in forecasting upcoming phreatic events. In this paper, we document PT results for the period 1990–2006 that, together with those of Rowe et al. (1992b), constitute a monitoring record of about 25 years. It will be shown that the PT budget in Laguna Caliente is characterized by a remarkable variability, which is directly linked to changes in the flow rate, composition and location of fumarole emissions within the crater

that hosts the lake. In conjunction with routinely monitored geochemical signatures, geophysical parameters and field observations, our findings provide new insights into the conditions of the subsurface magmatic-hydrothermal system, and the mechanisms that control eruptive events.

2 Sampling Strategy and Analytical Procedures

2.1 Sampling

Selected samples for PT analysis were routinely collected on the NE side of the acidic crater lake (Fig. 1). Most samples were stored in dark high-density polyethylene bottles at ambient temperature without filtration, dilution or addition of preservatives before carrying out the PT analyses. The available PT record covers the period 1980–2006 and represents an approximate sampling frequency of once every two months.

2.2 Polythionate Analysis

About 190 lake water samples were analyzed for tetra-, penta-, and hexathionate ions at the Department of Chemistry of Tokyo University (Japan) and at the Laboratory of Atmospheric Chemistry (LAQAT) of the Universidad Nacional (Costa Rica) using similar ion-pair chromatographic techniques described in the supplementary data to this article and described at http://www.ovsicori.una.ac.cr/index.php/vulcanologia/geoquimica/investigacion-geoquimica.

Overall deviations from the mean values were better than 20% RSD (3–20% for tetra-; 2–15% for penta-, and 1–20% for hexathionate. As most analyses in Tokyo and Costa Rica were carried out with time differences of about 3 years, it is possible to state that the PT time series presented in this chapter are largely unaffected by potential inter-laboratory differences or chemical instability. Repetition of sulfate and chloride analyses suggested that some of the oldest samples might have experienced a certain degree of evaporation

or mineral precipitation during storage. On the basis of the recorded increasing concentrations of SO_4 and Cl, those of PTs may have raised in these cases by 15–20% at most.

2.3 Determination of Major Anions, Dissolved Gases, PH and Other Solutes

All of the samples collected were analyzed for sulfate, chloride and fluoride by suppressed ion chromatography, using a fully automated microbore ion suppressed Dionex chromatographic sytem at the Laboratory of Volcano Geochemistry "Dr. Eduardo Malavassi Rojas" of OVSICORI Universidad Nacional (Costa Rica) (Martínez 2008). Based on the analysis of a synthetic solution, precision was about 0.1, 0.3 and 4% for sulfate, chloride, fluoride, respectively. Detection limits were 0.3, 0.1 and 0.05 mg/kg, respectively.

Dissolved unreacted SO_2 and H_2S gases in the lake water were measured in situ on an irregular basis during 1999–2006, using a gas detection tube method (Takano et al. 2008). Detection limits for dissolved SO_2 and H_2S were 1 and 0.2 ppm, respectively.

The pH measurements were performed on untreated samples at ambient temperature $(24 \pm 2\ °C)$ in the OVSICORI geochemistry laboratory using a WTW Multi 340i potentiometer. Combination of the new results with previously available data (e.g. Casertano et al. 1985; Rowe et al. 1992a, b; Nicholson et al. 1992, 1993; Martínez et al. 2000) constitutes a record for major anion concentrations, pH and temperature that covers the period 1980–2006.

All field-related data (lake volume, temperature, color, seismic records, etc.) are from the database of OVSICORI (Venzke et al. 2002; Martínez et al. 2000; Martínez 2008). Most monthly rainfall data are from the Poás volcano summit rain gauge of the Centro de Servicios y Estudios Básicos de Ingeniería of Instituto Costarrincense de Electricidad ICE located at 2,564 m a.s.l.

Table 1 Polythionate and major anion concentrations (mg/kg) of Poás crater lake for the period 1980–2006

Date	Temp. (°C)	pH_{lab} 24 ± 2 °C	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$	Total $S_xO_6^{2-}$	$S_4O_6^{2-}/S_5O_6^{2-}$	$S_4O_6^{2-}/S_6O_6^{2-}$	S_4O^{2-}	Cl^-	F^-	PT lab
Stage II												
31-Oct-80	45	0.11	190	270	130	590	0.7	1.5	65,500	26,900	1,320	(1)
28-Nov-84	48	0.07	83	410	100	593	0.2	0.9	57,700	23,700	1,500	(2)[a]
24-Jan-85	44	0.14	1,190	2,120	770	4,080	0.6	1.5	49,500	25,400	1,660	(2)[a]
20-Mar-85	44	0.13	1,120	1,760	510	3,390	0.6	2.2	48,200	24,700	15,60	(2)[a]
06-May-85	44	0.14	450	1,180	360	1,990	0.4	1.3	55,000	22,000	1,400	(2)[a]
22-Aug-85	45	0.17	970	1,740	520	3,230	0.6	1.8	54,200	21,100	1,280	(2)[a]
09-Oct-85	45	0.18	600	1,270	460	2,330	0.5	1.3	52,900	20,700	1,260	(2)[a]
04-Feb-86	39	0.26	1,160	1,420	520	3,100	0.8	2.2	36,900	16,500	1,010	(2)[a]
Stage III												
02-May-86	38	0.20	1,730	1,810	630	4,170	1.0	2.7	40,100	16,500	970	(2)[a]
23-Aug-86	52	0.20	1,700	1,700	520	3,920	1.0	3.3	41,200	18,900	1,020	(2)[a]
31-Oct-86	54	0.14	1,040	1,310	420	2,770	0.8	2.5	52,000	23,200	1,240	(2)[a]
10-Jan-87	58	−0.01	1,560	1,370	620	3,550	1.1	2.5	64,400	30,400	1,590	(2)[a]
27-Feb-87	62	−0.03	170	630	120	920	0.3	1.4	78,600	33,700	1,750	(2)[a]
19-Mar-87	62	0.00	53	70	b.d.l.	123	0.8	n.a.	82,900	35,900	1,820	(2)[a]
27-July-87	68	−0.27	2	6	b.d.l.	8	0.3	n.a.	103,000	44,900	2,110	(2)[a]
10-Sep-87	65	−0.23	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	108,000	43,400	2,060	(2)[a]
27-Nov-87	60	−0.24	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	101,000	48,000	1,910	(2)[a]
16-Jan-88	64	−0.37	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	127,000	59,300	2,250	(2)[a]
02-Mar-88	60	−0.31	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	118,000	51,300	2,100	(2)[a]
24-June-88	65	−0.61	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	175,000	73,100	2,970	(2)[a]
02-Sep-88	65	−0.53	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	196,000	44,200	3,810	(2)[a]
26-Oct-88	65	−0.43	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	192,000	47,400	4,220	(2)[a]
07-Feb-89	75	−0.87	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	286,000	28,000	10,400	(2)[a]
03-Mar-89	82	−0.55	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	233,000	27,200	6,310	(2)[a]

(continued)

Table 1 (continued)

Date	Temp. (°C)	pH_{lab} 24 ± 2 °C	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$	Total $S_xO_6^{2-}$	$S_4O_6^{2-}/S_5O_6^{2-}$	$S_4O_6^{2-}/S_6O_6^{2-}$	SO_4^{2-}	Cl^-	F^-	PT lab
31-May-89	85	−0.09	110	6	b.d.l.	116	18	n.a.	124,000	25,100	6,150	(2)[a]
22-June-89	80	−0.44	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	175,000	40,600	8,420	(2)[a]
26-July-89	82	−0.55	250	90	25	365	2.9	10	175,000	46,500	8,600	(2)[a]
17-Aug-89	87	−0.36	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	99,300	39,200	7,230	(2)[a]
24-Oct-89	85	−0.56	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	154,000	64,100	7,910	(2)[a]
26-Jan-90	78	−0.29	22	20	b.d.l.	42	1.2	n.a.	109,000	52,000	6,400	(2)[a]
21-Feb-90	85	−0.56	16	10	b.d.l.	26	1.5	n.a.	103,000	95,200	8,460	(2)[a]
17-Mar-90	75	−0.60	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	165,000	63,100	8,730	(2)[a]
01-June-90	83	−0.46	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	67,800	36,600	9,440	(1)
10-July-90	94	−0.44	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	85,600	79,600	15,400	(1)
13-Sep-90	88	−0.70	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	90,300	114,000	25,400	(1)
08-Dec-90	73	n.d.	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	34,800	40,800	4,860	(1)
08-Feb-91	65	−0.40	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	32,000	52,400	5,930	(1)
19-Apr-91	78	−0.42	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	43,600	50,700	5,610	(1)
26-July-91	63	−0.38	90	110	20	220	0.8	4.5	51,300	47,900	4,310	(1)
24-Sep-91	71	−0.44	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	67,800	55,800	6,320	(1)
21-Oct-91	74	n.d.	8	16	9	33	0.5	0.9	70,000	58,500	6,560	(1)
01-Nov-91	70	−0.50	9	b.d.l.	b.d.l.	9	n.a.	n.a.	72,100	61,100	6,790	(1)
12-Dec-91	64	−0.30	105	130	73	308	0.8	1.4	40,700	35,800	4,690	(1)
17-Jan-92	67	−0.50	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	75,000	58,700	5,750	(1)
07-Feb-92	67	−0.60	75	100	37	212	0.8	2.1	41,600	32,900	3,700	(1)
13-Mar-92	65	−0.70	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	119,000	87,400	8,800	(1)
03-Apr-92	75	−0.80	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	147,000	102,000	11,000	(1)
24-July-92	70	−0.60	12	b.d.l.	b.d.l.	12	n.a.	n.a.	94,200	67,800	8,260	(1)
21-Aug-92	75	−0.60	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	78,900	63,300	6,870	(1)
18-Sep-92	70	−0.60	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	93,100	74,400	8,390	(1)

(continued)

Table 1 (continued)

Date	Temp. (°C)	pH_{lab} 24 ± 2 °C	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$	Total $S_xO_6^{2-}$	$S_4O_6^{2-}/S_5O_6^{2-}$	$S_5O_6^{2-}/S_6O_6^{2-}$	S_4O^{2-}	Cl^-	F^-	PT lab
07-Oct-92	75	−0.50	30	24	20	74	1.1	1.2	52,400	71,600	5,060	(1)
19-Nov-92	80	−0.50	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	38,400	73,000	5,720	(1)
23-Jan-93	65	0.00	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	56,100	54,000	4,510	(2)
25-Feb-93	65	0.00	160	196	110	466	0.8	1.4	58,000	56,200	n.d.	(2)
02-Apr-93	60	0.00	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	65,000	75,500	7,550	(2)
09-Sep-93	64	0.35	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	50,400	29,600	5,840	(1)
22-Oct-93	60	0.00	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	46,000	27,600	5,330	(2)
12-Mar-94	55	0.00	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	83,100	56,500	7,780	(2)
23-Sep-94	65	−0.18	1,020	530	850	2,400	1.9	1.2	27,000	24,000	2,660	(1)
21-Oct-94	60	0.14	3,700	2,660	990	7,350	1.4	3.7	17,000	8,470	1,220	(2)
15-Nov-94	55	0.38	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	11,000	7,640	n.d.	(1)
06-Jan-95	50	0.22	2,700	1,530	900	5,130	1.7	3.0	16,000	10,200	1,060	(1)
03-Feb-95	47	0.18	2,340	1,420	880	4,640	1.6	2.7	16,600	10,100	990	(1)
10-Mar-95	42	0.68	1,800	1,230	500	3,530	1.5	3.6	20,500	7,780	950	(2)
Stage IV												
08-Sep-95	34	1.10	294	290	140	724	1.0	2.2	8,710	5,440	530	(2)
20-Oct-95	30	1.21	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	6,230	3,800	190	(2)
05-Jan-96	29	1.22	40	80	36	156	0.5	1.0	9,060	3,590	200	(2)
23-Feb-96	26	1.55	244	75	40	359	3.3	6.4	4,480	2,630	140	(2)
22-Mar-96	30	1.50	290	130	66	486	2.3	4.3	6,270	3,370	200	(2)
26-Apr-96	36	1.50	315	110	80	505	2.9	3.9	5,290	3,910	200	(2)
10-May-96	42	1.45	450	170	84	704	2.7	5.4	5,180	4,020	330	(2)
14-June-96	45	1.35	690	330	170	1,190	2.1	4.0	7,000	4,390	330	(2)
24-July-96	36	1.75	520	290	110	920	1.8	4.6	7,520	4,460	270	(2)
08-Aug-96	35	1.45	240	180	90	510	1.3	2.8	6,970	4,510	360	(2)
27-Sep-96	40	1.65	580	270	120	970	2.2	4.7	6,780	4,320	220	(2)

(continued)

Table 1 (continued)

Date	Temp. (°C)	pH_{lab} 24 ± 2 °C	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$	Total $S_xO_6^{2-}$	$S_4O_6^{2-}/S_5O_6^{2-}$	$S_4O_6^{2-}/S_6O_6^{2-}$	SO_4^{2-}	Cl^-	F^-	PT lab
28-Nov-96	31	1.55	580	310	96	986	1.9	6.0	6,790	5,110	300	(2)
18-Dec-96	29	1.13	310	170	80	560	1.8	3.8	4,870	3,650	260	(2)
07-Jan-97	32	1.40	490	240	100	830	2.0	4.8	6,880	5,750	290	(2)
04-Feb-97	31	1.40	360	170	100	630	2.1	3.5	5,110	3,850	310	(2)
03-Mar-97	29	1.18	230	130	90	450	1.8	2.6	4,410	3,260	170	(2)
17-Apr-97	27	1.40	270	150	80	500	1.7	3.3	4,640	4,230	230	(2)
14-May-97	29	1.45	510	200	70	780	2.5	7.2	4,640	4,420	310	(2)
04-June-97	32	1.50	610	250	60	920	2.5	10	4,750	4,280	230	(2)
02-July-97	32	1.50	500	200	75	775	2.5	6.7	4,870	4,620	210	(2)
22-Aug-97	31	1.45	700	270	60	1,030	2.6	12	5,770	6,690	200	(2)
05-Sep-97	35	1.30	590	260	50	900	2.3	12	4,060	4,330	170	(2)
17-Oct-97	34	1.06	790	280	56	1,126	2.9	14	7,840	6,520	360	(2)
04-Nov-97	35	1.40	810	280	64	1,154	2.9	13	6,460	7,800	280	(2)
06-Feb-98	38	0.90	840	420	115	1,375	2.0	7.3	7,910	7,920	420	(2)
25-Mar-98	37	0.79	990	430	110	1,530	2.3	9.1	9,120	9,440	490	(2)
17-Apr-98	37	0.68	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	10,900	8,870	460	(2)
15-May-98	36	0.64	810	370	120	1,300	2.2	6.8	11,500	12,400	620	(2)
25-June-98	36	0.99	260	170	35	465	1.6	7.4	7,500	6,490	500	(2)
30-July-98	35	0.73	890	490	160	1,540	1.8	5.7	10,800	11,800	600	(2)
26-Aug-98	35	0.73	890	420	120	1,430	2.1	7.3	7,970	8,410	390	(2)
21-Sep-98	35	0.74	850	400	110	1,360	2.1	7.6	9,850	10,800	550	(2)
04-Nov-98	35	0.85	350	190	110	650	1.9	3.3	8,140	8,740	480	(2)
23-Dec-98	27	0.90	330	170	80	580	1.9	4.0	7,650	7,840	600	(2)
13-Jan-99	32	0.77	430	210	130	770	2.1	3.4	9,110	9,890	640	(2)
25-Feb-99	33	0.68	470	220	110	800	2.1	4.2	10,600	11,700	660	(2)
17-Mar-99	32	0.81	460	180	120	760	2.5	3.9	9,760	10,900	720	(2)

(continued)

Table 1 (continued)

Date	Temp. (°C)	pH_{lab} 24 ± 2 °C	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$	Total $S_xO_6^{2-}$	$S_4O_6^{2-}/S_5O_6^{2-}$	$S_4O_6^{2-}/S_6O_6^{2-}$	SO_4^{2-}	Cl^-	F^-	PT lab
21-Apr-99	32	0.72	380	200	150	730	1.9	2.6	10,400	11,300	800	(1)
07-May-99	34	0.71	360	200	150	710	1.8	2.4	10,700	11,600	810	(1)
18-June-99	34	0.68	330	130	90	550	2.6	3.7	8,550	7,510	480	(1)
07-July-99	32	0.68	300	170	140	610	1.7	2.1	11,100	12,200	720	(1)
19-Aug-99	35	0.81	290	150	110	550	2.0	2.6	10,200	11,200	720	(1)
08-Sep-99	39	0.62	290	130	90	510	2.2	3.2	8,220	8,120	660	(1)
22-Oct-99	38	0.61	290	190	140	620	1.5	2.1	12,100	13,300	920	(1)
05-Nov-99	39	0.80	380	140	100	620	2.7	3.7	9,250	9,130	730	(1)
27-Dec-99	34	0.72	300	200	140	640	1.5	2.1	10,400	11,400	790	(1)
21-Jan-00	38	0.76	240	100	62	402	2.3	3.9	9,270	9,850	740	(1)
10-Feb-00	44	0.69	210	100	60	370	2.0	3.5	10,200	10,800	830	(1)
13-Mar-00	36	0.71	120	65	50	235	1.9	2.5	9,270	9,620	700	(1)
11-Apr-00	32	0.74	230	110	66	406	2.0	3.4	9,780	10,400	830	(1)
05-May-00	31	0.67	200	100	53	353	2.0	3.8	8,330	8,280	810	(1)
09-June-00	31	0.77	210	97	87	394	2.1	2.4	9,260	11,900	710	(1)
17-July-00	33	0.74	110	52	30	192	2.1	3.7	7,230	9,050	510	(1)
24-Aug-00	31	0.60	150	90	57	297	1.6	2.6	9,240	13,300	700	(1)
12-Sep-00	35	0.60	190	87	62	339	2.2	3.1	9,410	12,700	620	(1)
10-Oct-00	35	0.70	180	84	52	316	2.2	3.5	8,900	11,700	580	(1)
21-Nov-00	34	0.71	160	76	40	276	2.0	4.0	8,930	11,900	670	(1)
01-Dec-00	34	0.90	160	72	50	282	2.2	3.3	8,320	10,900	610	(1)
12-Jan-01	31	0.86	120	80	78	278	1.6	1.6	8,700	11,400	680	(1)
23-Feb-01	31	0.83	120	80	97	297	1.6	1.3	7,870	9,670	540	(1)
08-Mar-01	32	0.65	130	79	38	247	1.7	3.5	9,080	11,600	710	(1)
26-Apr-01	35	0.75	120	66	25	211	1.8	4.7	9,400	11,700	660	(1)
08-May-01	34	0.70	160	80	80	320	2.0	2.0	9,080	12,200	690	(1)

(continued)

Table 1 (continued)

Date	Temp. (°C)	pH_{lab} 24 ± 2 °C	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$	Total $S_xO_6^{2-}$	$S_4O_6^{2-}/S_5O_6^{2-}$	$S_4O_6^{2-}/S_6O_6^{2-}$	SO_4^{2-}	Cl^-	F^-	PT lab
13-June-01	35	0.67	150	74	84	308	2.0	1.8	9,100	11,700	560	(1)
19-July-01	28	0.70	190	70	34	294	2.7	5.5	7,270	8,400	460	(1)
03-Aug-01	24	0.85	160	74	72	306	2.2	2.2	8,090	9,760	510	(1)
07-Sep-01	27	0.39	360	110	80	550	3.3	4.6	8,510	9,590	540	(1)
18-Oct-01	28	0.85	360	160	105	625	2.2	3.4	7,800	8,280	380	(1)
27-Nov-01	30	1.07	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	3,450	2,720	82	(1)
07-Dec-01	30	1.43	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	3,310	2,830	67	(1)
31-Jan-02	30	1.51	6	10	9	25	n.a.	n.a.	3,590	2,540	52	(1)
27-Feb-02	23	1.17	9	14	12	35	0.6	0.7	6,050	4,670	160	(1)
13-Mar-02	26	1.06	33	50	7	90	0.6	4.7	6,390	5,760	190	(1)
03-Apr-02	25	1.04	53	80	14	147	0.7	3.8	6,830	6,420	380	(1)
16-May-02	29	1.08	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	6,060	6,260	230	(1)
11-June-02	29	0.90	67	50	37	154	1.3	1.8	5,060	5,780	130	(1)
30-July-02	32	0.99	140	52	30	222	2.7	4.8	6,800	7,620	320	(1)
04-Sep-02	38	0.90	580	220	70	870	2.7	8.4	7,660	8,720	300	(1)
11-Dec-02	39	0.84	620	280	63	963	2.2	9.9	8,510	10,700	430	(2)
17-Jan-03	34	0.83	460	300	138	898	1.5	3.3	8,780	10,500	480	(2)
28-Feb-03	36	0.77	600	380	143	1,123	1.6	4.2	8,870	10,900	520	(2)
31-Mar-03	39	0.70	940	460	143	1,543	2.1	6.6	9,360	15,000	580	(2)
30-Apr-03	41	0.67	910	560	170	1,640	1.6	5.3	10,500	16,100	620	(2)
20-May-03	41	0.70	810	470	180	1,460	1.7	4.5	11,000	16,200	620	(2)
17-July-03	35	0.64	400	380	184	964	1.1	2.2	11,800	17,100	650	(2)
12-Aug-03	33	0.61	720	450	148	1,318	1.6	4.9	8,860	18,200	720	(2)
30-Sep-03	33	0.62	280	240	112	632	1.2	2.5	13,800	15,300	560	(2)
28-Oct-03	28	0.80	6	4	b.d.l.	10	1.5	n.a.	9,290	12,700	320	(2)
05-Dec-03	24	0.93	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	6,100	8,310	240	(2)

(continued)

Table 1 (continued)

Date	Temp. (°C)	pH_{lab} 24 ± 2 °C	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$	Total $S_xO_6^{2-}$	$S_4O_6^{2-}/S_5O_6^{2-}$	$S_4O_6^{2-}/S_6O_6^{2-}$	$S_2O_3^{2-}$	Cl^-	F^-	PT lab
20-Jan-04	24	1.17	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	5,260	6,670	180	(2)
03-Feb-04	29	1.11	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	4,550	5,880	190	(2)
23-Mar-04	25	1.05	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	5,290	6,530	180	(2)
27-Apr-04	28	1.12	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	5,300	6,330	160	(2)
25-May-04	28	1.31	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	3,940	5,380	26	(2)
11-June-04	29	1.20	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	4,540	6,480	65	(2)
01-July-04	26	1.24	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	5,680	5,320	n.d.	(2)
12-Aug-04	25	1.10	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	7,690	6,320	170	(2)
22-Sep-04	29	1.16	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	7,170	5,860	140	(2)
22-Oct-04	27	1.08	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	7,940	6,920	160	(2)
2-Dec-04	23	1.17	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	7,750	5,930	130	(2)
22-Feb-05	22	1.25	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	3,780	3,680	92	(2)
Stage V												
21-Mar-05	32	1.22	b.d.l.	b.d.l.	b.d.l.	n.a.	n.a.	n.a.	4,670	5,330	130	(2)
12-Apr-05	34	0.97	190	110	10	310	1.6	21	7,340	6,570	220	(2)
4-May-05	41	1.02	470	120	30	620	3.9	15	8,120	6,900	260	(2)
24-June-05	50	0.92	1,160	360	70	1,590	3.3	16	9,310	8,380	470	(2)
14-July-05	50	0.79	540	250	110	900	2.2	4.8	9,900	8,800	530	(2)
24-Aug-05	51	0.75	860	470	172	1,502	1.9	5.0	11,400	10,200	690	(2)
20-Sep-05	52	0.70	1,100	820	270	2,190	1.3	4.1	12,800	11,100	750	(2)
30-Nov-05	54	0.64	1,850	1,390	410	3,650	1.3	4.5	13,600	11,600	920	(2)
31-Jan-06	51	0.65	1,620	1,310	500	3,430	1.2	3.2	15,700	12,000	870	(2)
28-Feb-06	51	0.59	760	670	280	1,710	1.1	2.8	17,700	13,400	990	(2)
1-Apr-06	54	0.63	710	500	275	1,485	1.4	2.6	17,200	15,700	1,050	(2)
25-May-06	47	0.72	90	100	48	238	0.9	1.8	19,500	15,900	1,130	(2)
22-June-06	46	0.59	110	100	50	260	1.1	2.3	23,100	16,300	1,090	(2)

(continued)

Table 1 (continued)

Date	Temp. (°C)	pH_{lab} 24 ± 2 °C	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$	Total $S_xO_6^{2-}$	$S_4O_6^{2-}/S_5O_6^{2-}$	$S_4O_6^{2-}/S_6O_6^{2-}$	S_4O^{2-}	Cl^-	F^-	PT lab
20-July-06	43	0.62	70	70	30	170	0.9	2.2	21,300	13,400	890	(2)
11-Aug-06	43	0.52	120	95	58	273	1.2	2.0	25,400	16,100	1,100	(2)
05-Sep-06	41	0.47	280	240	100	620	1.2	2.8	27,500	17,100	1,100	(2)
28-Oct-06	53	0.50	100	50	22	172	1.9	4.4	29,000	16,300	1,170	(2)
10-Nov-06	57	0.43	85	40	25	150	2.1	3.4	29,100	13,200	950	(2)

PT lab refers to laboratory where PTs were separated and analysed by chromatography: (1) Laboratory of Atmospheric Chemistry School of Chemistry Universidad Nacional, LAQAT-UNA Heredia; (2) Tokyo University

[a]Data from Rowe et al. (1992b); b.d.l.: below detection limit; n.d.: not determined; n.a.: not applicable

3 Results and Discussion

3.1 Polythionate Results

Analytical results of tetra-, penta-, and hexathionate are given in Table 1, together with the concentrations of sulfate, chloride and fluoride and other relevant parameters. For completeness, published data by Rowe et al. (1992b) are also included. As a consequence, Table 1 lists a PT record for the period October 1980–November 2006.

Many chromatograms showed two or three peaks that were eluted after the hexathionate ion, corresponding to higher homologues of PTs such as heptathionate ($S_7O_6^{2-}$), octathionate ($S_8O_6^{2-}$), and nonathionate ($S_9O_6^{2-}$) (Fig. 2) (cf. Steudel and Holdt 1986). Qualitative inspection of all chromatograms suggested that these long-chain PTs were present in the lake water during periods when the shorter homologues were abundant.

They were undetectable during periods when the latter were absent or present in low amounts. Higher PTs, including nona- and decathionate, were also detected in the acid crater lakes of Ruapehu (Takano et al. 1994b) and Kusatsu-Shirane (Takano 1987). Because long-chain PTs are more susceptible to thermal and sulfitolytic breakdown than the shorter PTs (Fujiwara et al. 1988; Takano et al. 2001, 2004), and because they are much less abundant and more difficult to be quantified, only the concentrations of the tetra-, penta-, and hexathionate are reported here. Thus, throughout this paper "total PTs" refers to the sum of concentrations of these three species.

Martínez (2008) distinguished five main stages of volcanic activity at Poás since the late 1970s, based on time-series trends for a set of geochemical and geophysical monitoring parameters (see also Rymer et al. 2009). Figures 3, 4 and 5 portray time series of PT concentrations, together
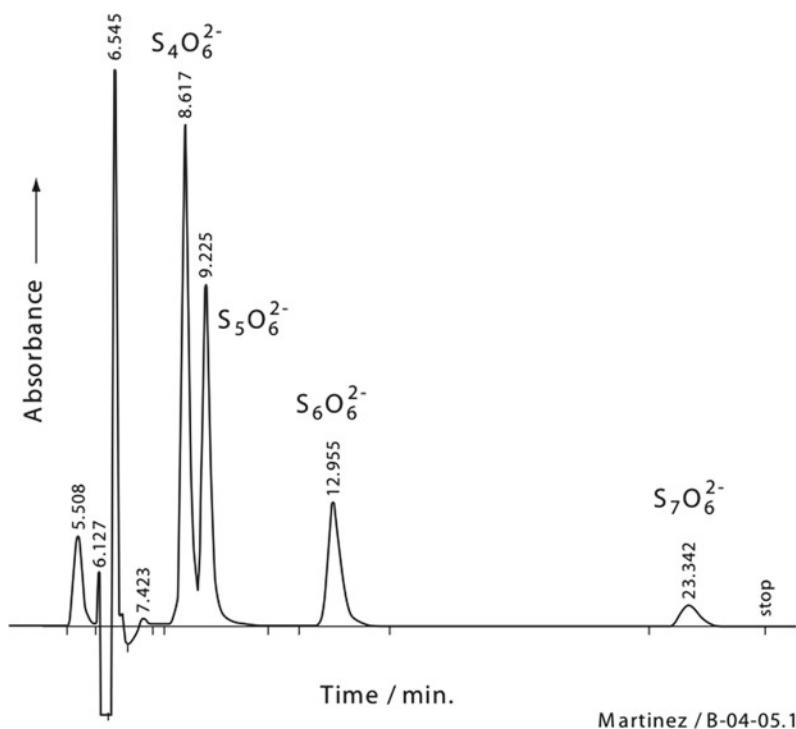
Fig. 2 Example of a chromatogram for a lake-water sample (collected on 21 August 1999) obtained at LAQAT, where separation and quantification of the thionates were performed following Miura and Kawaoi (2000). The sample was diluted 25 times by weighing. Peaks of tetrathionate, pentathionate, hexathionate and heptathionate are labeled. The peaks that eluted before tetrathionate are due to unknown impurities in the sample
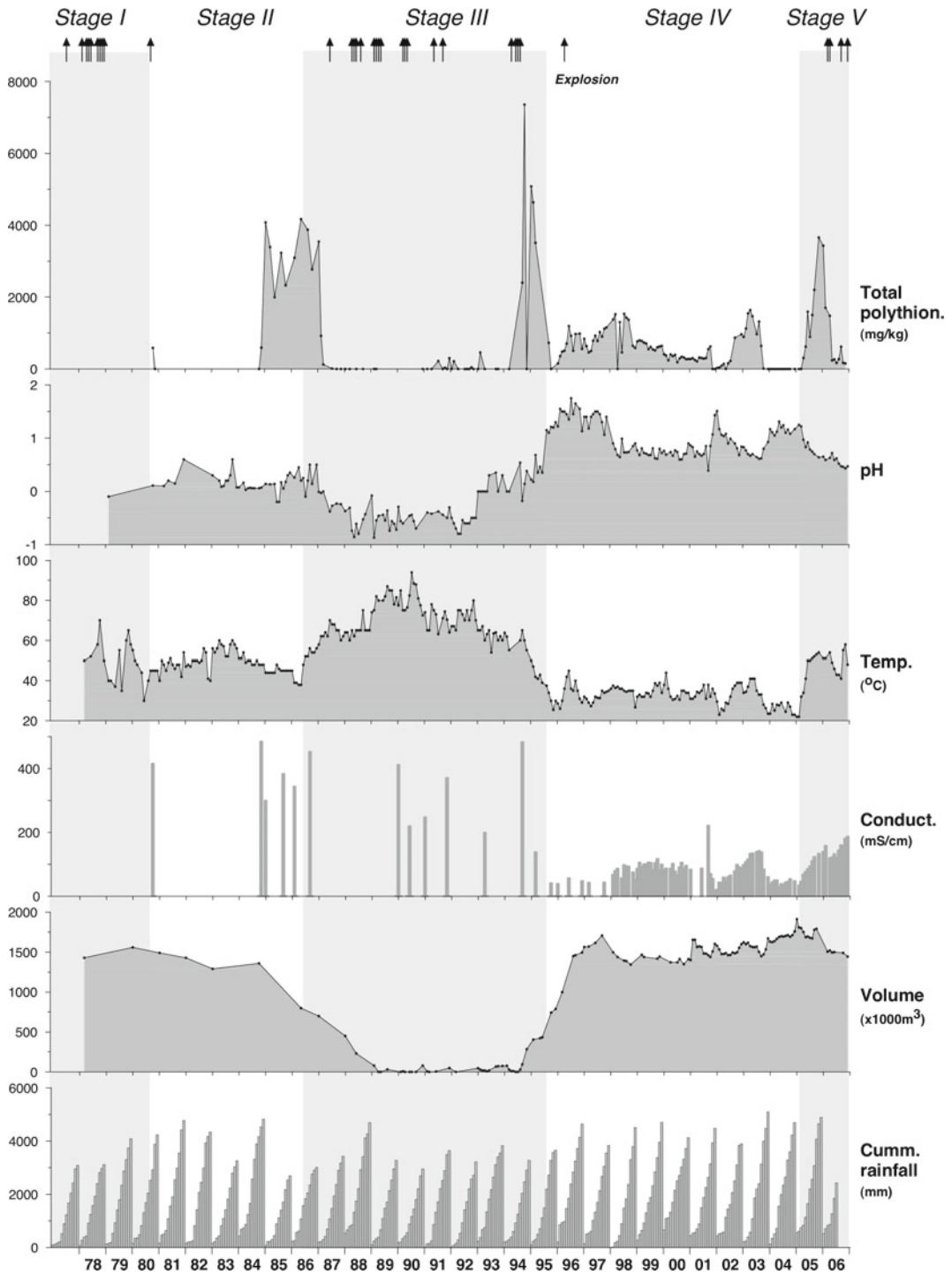
Fig. 3 Time series of total PT concentrations (sum of tetra-, hexa- and pentathionate), pH, temperature, conductivity and volume of the crater lake between 1978 and 2006. Rainfall registered at the summit of Poás (ICE's pluviometer) is expressed as cumulative monthly totals in cycles of calendar years. Arrows on top of the graph indicate phreatic eruptions and a minor hydrothermal explosion at the northern side of the dome that occurred on April 8, 1996, presumably as a result of unclogging of fumarolic vents
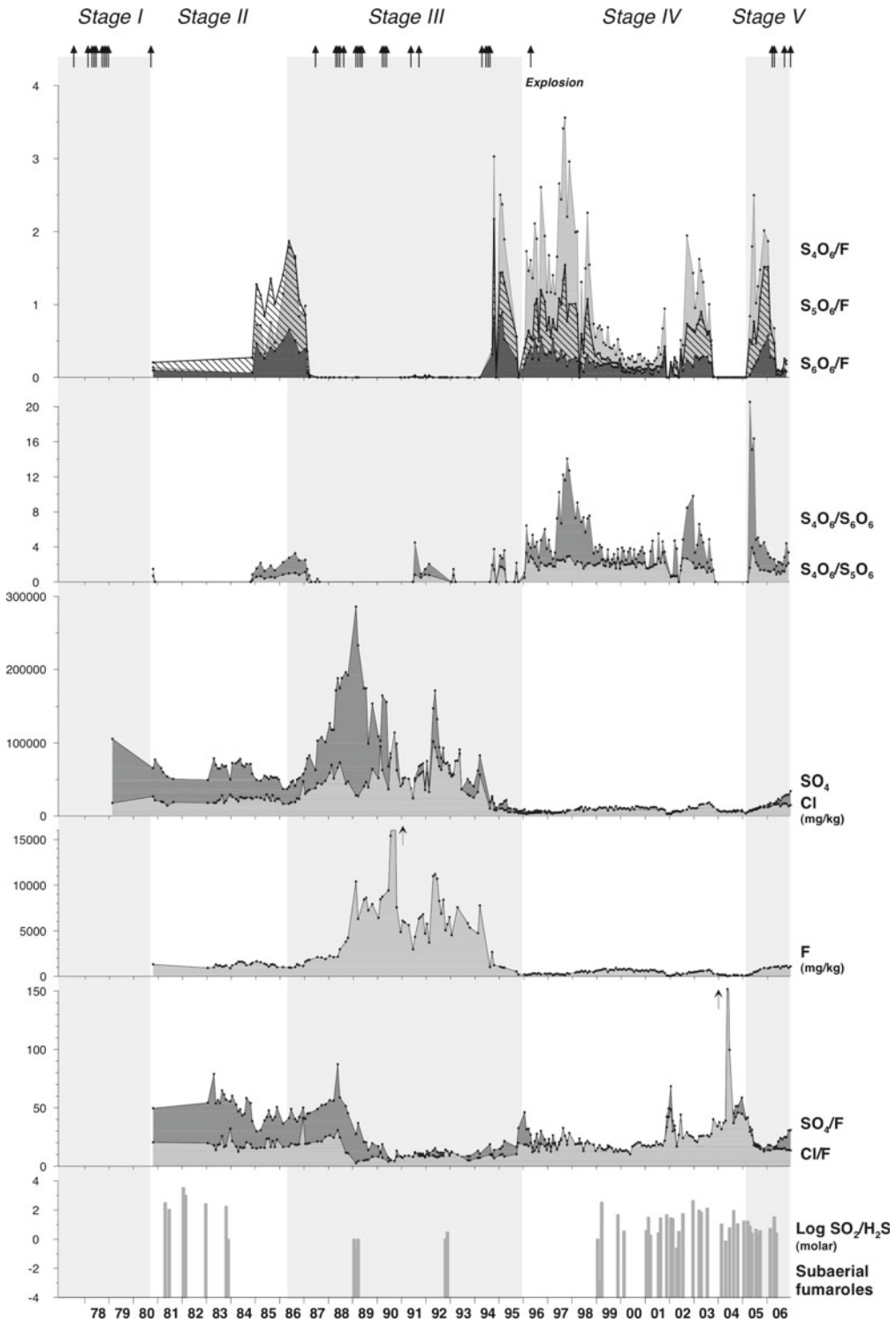
Fig. 4 Time series of PT concentrations normalized to fluoride, S_4O_6/S_5O_6 and S_4O_6/S_6O_6 ratios, concentrations (mg/kg) and ratios of major anions, as well as molar SO_2/H_2S ratios of sub-aerial fumaroles. Except for the latter, all ratios are wt/wt. Arrows on top of the graph indicate phreatic eruptions. Arrows in the F and Cl/F panels indicate values that are out of scale
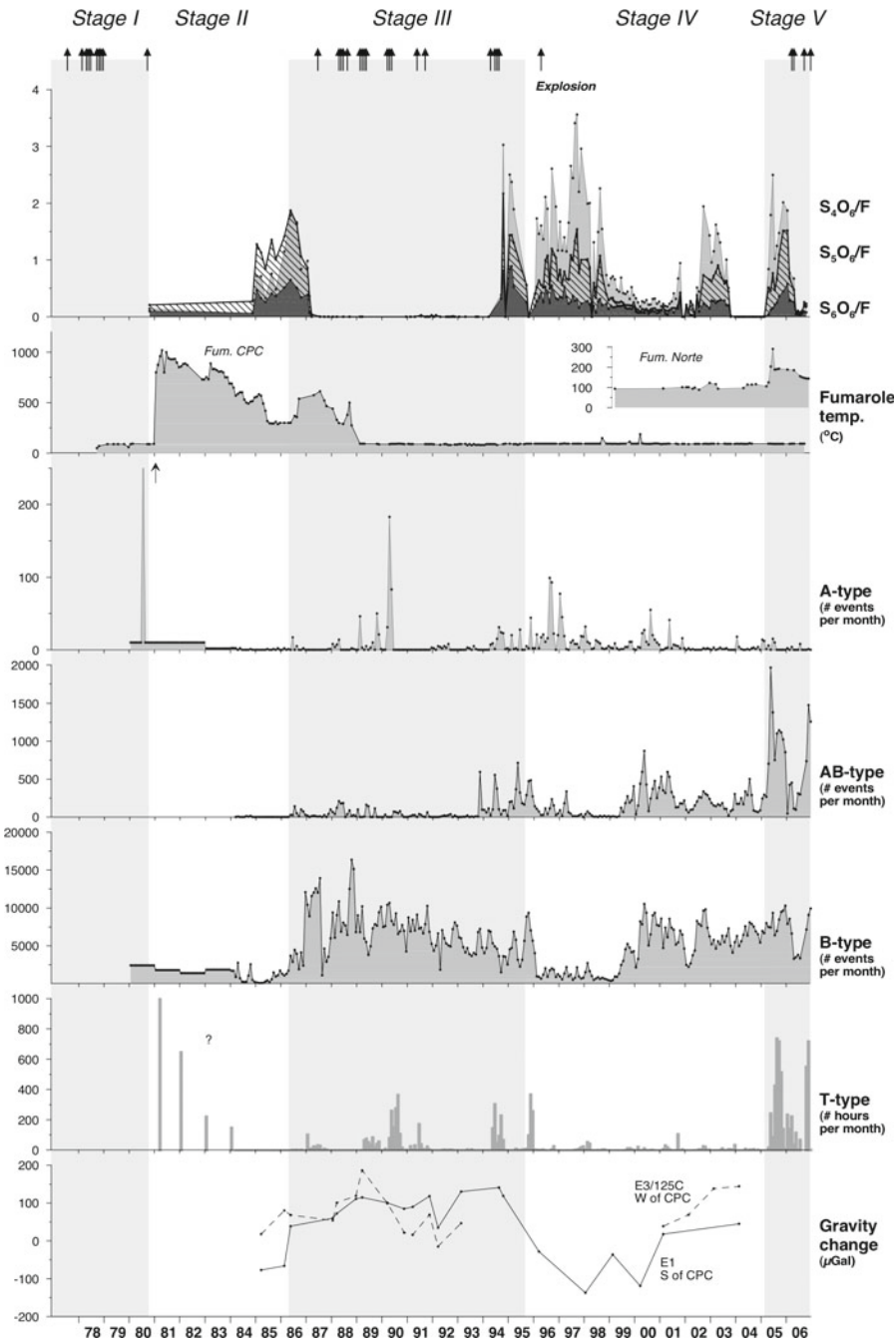
Fig. 5 Time series of F-normalized PT concentrations compared with fumarole temperatures, seismicity and microgravity changes monitored at Poás volcano. Seismicity is distinguished according to A, AB, B and tremor (T)-type characteristics, and is expressed as numbers of monthly events, except for T-type seismicity, which is given in hours per month. Arrow in the A-type panel refers to July 1980 when recorded quakes numbered in the thousands within a two-week period (Casertano et al. 1985). Peaks in volcanic tremor were registered between

March 1981 and 1983 but the exact number of monthly hours are unknown (question mark in T-type panel). They coincided with very high temperatures of the dome fumaroles (700–1020 °C), which produced an SO_2 flux of about 800 tons per day (Casadevall et al. 1984b; Fernández 1990). Microgravity data (Rymer et al. 2005) are shown for two stations near the dome and reflect changes relative to a base station 7 km from the crater, normalized to the difference observed in 1987. Arrows on top of the graph indicate months with phreatic eruptions

with key chemical and physical properties of the lake, fumarole temperatures and seismicity observed during these stages. To eliminate potential dilutive or evaporative effects, the PT concentrations are normalized against fluoride rather than chloride or sulfate, because the former behaves conservatively, whereas HCl exerts significant vapor pressure and is easily distilled from acidic lake brines under conditions of high acidity and relatively low temperature, such it was observed in mid 1988-early 1989 (Rowe et al. 1992b) and 1998-late 2003 (Martínez 2008). On the other hand, sulfate tends to precipitate as a solid assemblages (e.g. gypsum/anhydrite, hydrous aluminium sulphates) in saturated to oversaturated lake brines.

The PTs formed a significant part of the anion budget during the transitional period between Stages II and III, and from the end of Stage III on through most of Stages IV and V (Figs. 3, 4, and 5), when concentrations reached several hundreds or thousands of milligrams per kilogram. Commonly, the analyzed species showed $S_4O_6^{2-} > S_5O_6^{2-} > S_6O_6^{2-}$ as concentration sequence (Table 1; Figs. 4, 5 and 6). However, during Stage II and the first fourteen months of Stage III the sequence was $S_5O_6^{2-} > S_4O_6^{2-} > S_6O_6^{2-}$ (Rowe et al. 1992b). This distribution was also observed during brief intervals of relative quiescence in the lake: mid 1991-early 1992, mid 1995–January 1996, the first four months of 2002 and May–July 2006, when overall PT concentrations tended to be rather low (Table 1).

3.2 Polythionates: Relationships with Lake Properties, Fumarolic Activity and Eruptive Phreatic Events

In the following sections, variations in terms of PT distributions are described in relation to the composition and behavior of the lake, on-shore fumarolic activity, eruptive phreatic events and monitored seismicity for the lake activity stages as recognized by Martínez (2008). Since no polythionate data are available for Stage I, the overview will commence with Stage II.

3.2.1 Stage II (September 1980–April 1986): High PT Concentrations, Moderate Convective Activity in the Lake Without Phreatic Eruptions, High-Temperature Degassing Through the Dome

During the last part of Stage II the PT concentrations were distributed in the sequence $S_5O_6^{2-} > S_4O_6^{2-} > S_6O_6^{2-}$ (Rowe et al. 1992b). Single data points for October 1980 and November 1984 suggested that PTs were initially present in relatively low amounts (about 600 mg/kg). From early 1985 on, an irregularly increasing trend culminated in a maximum of total polythionates of about 4,170 mg/kg in May 1986 (Table 1; Fig. 3) was observed. This strong increase coincided with swarms of A-type seismicity (volcano-tectonic quakes) (peaking in June–August), and also marked the start of a period of elevated B-type seismicity (long-period quakes) in May (Fernández 1990; Rowe et al. 1992a), which continued throughout Stage III (Fig. 5). The observed lowering of the lake volume after 1985 was probably partly due to relatively low rainfall in 1985, 1986, and 1987 (Fig. 3), but increased heat input must have significantly contributed to a rapid decline in early-mid 1986 (Rowe et al. 1992a). A marked increase in lake temperature was not observed until June 1986 when 48 °C were measured, i.e. 10 °C higher than in the previous month (Fig. 3).

Trends of individual PT species were not entirely parallel. A conspicuous change in relative abundances was found in February and May 1986 when, compared to the other species, tetrathionate apparently had formed at much higher rates than what previously recorded. Pentathionate remained predominant throughout, but tetrathionate was present in almost equal amount at the peak levels of May 1986 (Fig. 4). As discussed in Rowe et al. (1992b), fluctuations in PT speciation and their stability in the lake reflected changes in the SO_2/H_2S ratio of subaqueous fumaroles. The observed distribution of

$S_5O_6^{2-} > S_4O_6^{2-} > S_6O_6^{2-}$ points to the predominance of H_2S-enriched subaqueous fumaroles with a molar SO_2/H_2S ratio of <0.07, which would favor the formation of pentathionate over tetrathionate (Fig. 7) (Takano et al. 1994b).

Despite the termination of phreatic eruptions by the end of 1980, several thousands of A-type seismic events were recorded between April and August 1980, which preceded an interval of strongly increased well-defined volcanic tremors between September 1980 and 1984 (Casertano et al. 1985; Fernández 1990). This enhanced seismicity coincided with a very high flux of high-temperatures gases (800–1,020 °C, Fig. 5) from the dome in January 1981–September 1983, producing a strong sulfurous odour (Malavassi and Barquero 1982; Barquero and Malavassi 1983). COSPEC measurements recorded SO_2 fluxes of about 800 tons/day in February 1982 (Barquero and Fernández 1983; Casadevall et al. 1984b). This vigorous release of hot SO_2-rich gas from the dome was possibly associated with the emplacement of a small magma body below it (Brown et al. 1991). If so, both the intrusion and the channeling of expelled volatiles must have been confined to the small area below the dome, because properties of the lake were not dramatically affected, as illustrated by the distribution of PT species pointing to an input of H_2S rather than SO_2-rich gas into the lake.

Casertano et al. (1987) suggested that, during maximum heating of the dome in 1981–1983, the lake was still in continuous hydraulic connection with the rising hot fluids, consistent with the steady increase in lake temperature in these years (see Fig. 3). The lake had temperatures around 50 °C, a grayish-turquoise color, and showed strong evaporation and streaks of floating sulfur globules. By the end of October 1983 the water level descended about 10 m (Fig. 3). The detected increase in the $S_4O_6^{2-}/S_5O_6^{2-}$ and $S_4O_6^{2-}/S_6O_6^{2-}$ ratios in 1985-mid 1986 can thus be explained by an increase in the SO_2/H_2S ratio of subaqueous fumaroles after October 1985 (Figs. 4 and 5). This change probably occurred in early 1986 when swarms of A-type earthquakes and elevated B-type seismicity were recorded, possibly induced by hydrofracturing of the magmatic carapace and subsequent release of magmatic volatiles (Rowe et al. 1992a, b). Episodes of harmonic tremor of short duration (<1 min) and low amplitude (<1 mm), which are rare at Poás and not yet well understood, were also recorded in early 1986 (Fernández 1990). Shallow intrusion of fresh magma batches as source of the enhanced SO_2 output was also envisaged from micro-gravity increases in the southern part of the active crater observed between 1985 and 1989 (Fig. 5) (Rymer et al. 2000, 2004, 2005).

3.2.2 Stage III (May 1986–August 1995): PTs in Trace Amounts or Absent, Frequent Phreatic Eruptions, Intense Fumarolic Degassing

After the peak levels of May 1986 PT concentrations showed a strong steady decrease concomitant with an increase in lake temperature, a decrease in pH and a reduction in lake volume (Fig. 3). By mid 1987 the lake temperature rose above 60 °C, the pH dropped to negative values, and the PT concentrations were below the detection limits. These effects roughly coincided with the first phreatic eruptions from the lake in June 1987 (Venzke et al. 2002; Rowe et al. 1992a). Since then, PTs remained undetected for most of Stage III; only occasionally minor amounts were measured (Fig. 3). By the end of Stage III, after cessation of phreatic eruptions in early August 1994, a new lake started to rise, the temperature dropped, the pH increased, and a significant amount of PTs were formed, as observed for the first time between October 1994 and February 1995. The initial recovery of the lake was characterized by high PT concentrations ($\Sigma S_xO_6^{2-}$ up to 7,350 mg/kg in October 1994), similar to those observed in May 1986. Irregular activity variations in the lake occurred in view of their temporary disappearance in November 1994 (Figs. 3 and 4).

If the occasional presence of PTs in the course of Stage III is taken into account, a generalized pattern for the PT distribution can be discerned. Available data between 1989 and early 1990
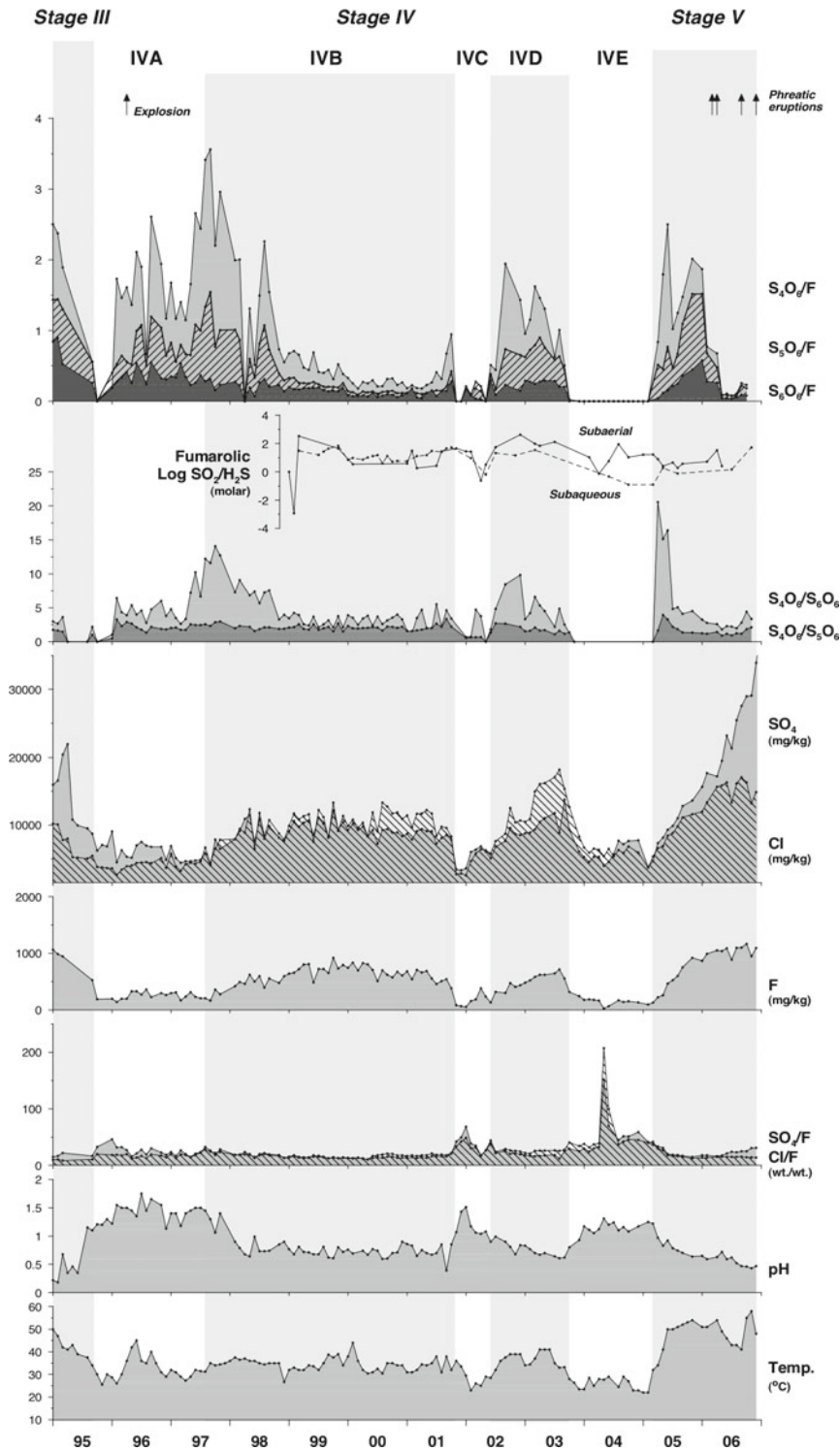
Fig. 6 Detailed time series of PT concentrations (normalized to fluoride) and ratios of other major anions (wt/wt) for part of Stage III, the Stage IV and the first years of Stage V, together with other crater-lake parameters and molar SO_2/H_2S ratios of sub-aerial (measured) and subaqueous (inferred, see text) fumaroles. Note the (near) absence of PTs at the beginning of sub-stage IVA and in sub-stages IVC and IVE, periods of relative quiescence in the lake, whereas the low concentrations of PTs after 2006 is rather related to enhanced fumarolic outgassing through the lake. Concentrations of anions are given in mg/kg
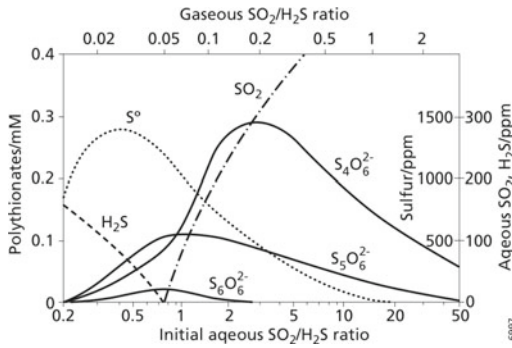
Fig. 7 Predicted distributions of PTs, elemental sulfur, SO_2 and H_2S in an aqueous solution. The SO_2/H_2S ratio of entering fumarolic gas (upper horizontal axis) controls the initial aqueous SO_2/H_2S ratio in solution (lower horizontal axis), which determines the distribution of PT species, elemental sulfur, and concentrations of any excess (unreacted) H_2S or SO_2 that remains in solution after PTs and elemental sulfur have formed (from Takano et al. 1994b)

showed a strong dominance of tetrathionate over the other species at very low overall concentrations. In contrast, pentathionate was overall the most abundant species in samples between mid-1991 and early 1993, whereas once again the distribution changed in favor of tetrathionate at the high $\Sigma S_x O_6^{2-}$ concentrations towards the end of Stage III (Table 1; Figs. 4, 5 and 6).

The breakdown of PTs at the beginning of Stage III was accompanied by an increase in the SO_4^{2-}/F^- ratios of lake samples till mid-1988 (Fig. 4). Although PT breakdown by thermal effects or otherwise will generally produce sulfate (Takano and Watanuki 1990; Takano et al. 2001), this process alone cannot account for the rise of SO_4^{2-} concentrations and SO_4^{2-}/F^{-1} ratios observed between May and July 1986. Moreover, the trend of increasing SO_4^{2-}/F^{-1} ratios in lake samples started already in mid-1985 (Fig. 4). Hence, increased input of hot SO_2-rich volatiles was likely responsible for most of the sulfate production, consistent with an increase in the SO_2/H_2S ratio of subaqueous fumaroles, as inferred from the change in the distribution of PT species since August 1986 (Fig. 4), albeit with temporary reversals in some of the late 1986 and early 1987 samples. The enhanced SO_2 input in August 1986 produced maximum

$S_4O_6^{2-}/ S_6O_6^{2-}$ ratios at low $\Sigma S_x O_6^{2-}$ concentrations in the first half of Stage III, presumably as a result of thermal breakdown and sulfitolysis reactions (Takano and Watanuki 1990; Takano et al. 2001), although for most part of Stage III PTs were absent. A plot of PT concentrations versus lake temperature shows that PTs reached maximum concentrations when the temperature ranged between 38 and 65 °C, and that they were not stable at >65 °C (Fig. 8). At Ruapehu Crater Lake, complete degradation of PTs occurred at temperatures above 47 °C (Takano et al. 1994b). Thus, both thermal and sulfitolytic decomposition were probably responsible for the disappearance of PTs in the Poás lake during Stage III.

Accompanied by a notable increase in B-type seismicity (Fig. 5), these changes in the lake geochemistry culminated in frequent, moderate to strong phreatic explosions, and strong subaqueous fumarolic degassing within the lake area, starting in June 1987 and continuing till the beginning of 1988. Phreatic activity intensified in early 1988 and continued until early 1989 when the lake disappeared, enabling for the first time the direct observation of large pools of molten
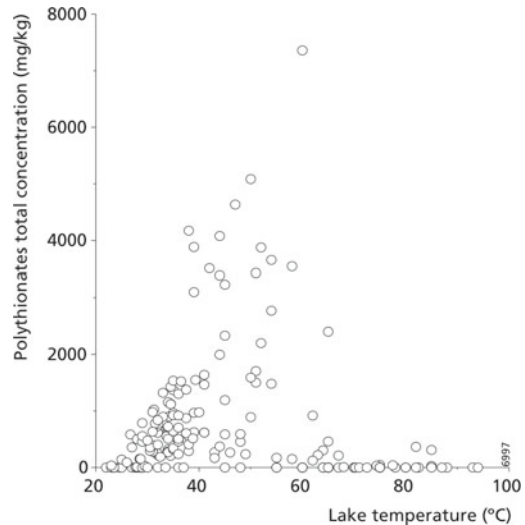
Fig. 8 Total PT concentrations versus lake temperature for the period October 1980–November 2006. Maximum concentrations were observed at temperatures between 38 and 65 °C, whereas higher temperatures result in the breakdown of PTs

sulfur and "sulfur volcanoes" on the dried lake bottom (Oppenheimer and Stevenson 1989). Subsequently, a series of strong phreatic explosions that ejected mud, sulfur, and lake sediments (some up to heights of ~2 km) occurred throughout 1989 and early 1991 (Venzke et al. 2002; Rowe et al. 1989), coinciding with periods of significant T-type seismic activity and A-type seismic swarms (A-type seismic signals were recorded together with T-type events in 1989 and 1990 but not in 1991) (Fig. 5). The strong phreatic activity and intense release of gases and steam reduced the lake to scattered mud pools during the dry seasons (April 1989, April 1990 and March 1991), and prevented it from reaching normal levels during rainy seasons. In addition, the yearly rainfall between 1989 and early 1991 (2,950–3,600 mm) was somewhat less than the average of ~4 m per year (Fig. 3).

The subsequent shift towards a PT distribution of $S_5O_6^{2-} > S_4O_6^{2-} > S_6O_6^{2-}$ (when they were detectable) and the inferred concomitant decrease in the SO_2/H_2S ratio of subaqueous fumaroles marked a period of noticeable lower activity in the lake area. Conditions of only moderate fumarolic degassing and absence of phreatic eruptions (Venzke et al. 2002; Barquero 1998) prevailed from mid-1991 throughout 1992 and 1993. The lake level rose to a maximum of several meters, especially during the rainy seasons of 1991 and 1993 when rainfall was relatively heavy (Fig. 3). Although the lake remained shallow, recorded water levels were higher than in the previous years (depths were ~5 m and 4 m in December 1991 and December 1993, respectively) (Barquero 1998; Venzke et al. 2002). Between mid-1991 and 1993 seismic activity was relatively low, with A-type and T-type (volcanic tremor) seismicity being virtually absent, and a slight decrease in the predominant B-type seismic events (Fig. 5). COSPEC measurements carried out in February 1991 showed an average flux of 91 tons of SO_2 per day (Andres et al. 1992).

As a prelude to renewed activity, the shallow lake evaporated at a rapid rate in early 1994, and was reduced once again to mud pools by March.

This desiccation was preceded by an increase in AB-type seismicity (long period medium-frequency quakes, $f = 2.1–3.0$ Hz) in November 1993, and was accompanied by increases in A-type, AB-type, and B-type seismicity. Between June and early August 1994 numerous strong phreatic explosions and strong release of gas and steam occurred within the lake area. Occasionally, a large water-rich plume rose to heights of more than 2,000 m above the crater floor. The largest phreatic explosions were registered in the second half of July (Venzke et al. 2002; Martínez et al. 2000). Swarms of A-type, AB-type, and numerous T-type seismic events preceded or accompanied this explosive activity (Fig. 5), which was further marked by sulfur combustion (suggesting temperatures ≥ 248 °C, the auto-ignition temperature of elemental sulfur) and high-temperature fumaroles (up to about 700 °C) at the dried lake bottom (Barquero 1998; Venzke et al. 2002).

The increase in seismicity, heat and volatile fluxes that triggered the mid-1994 phreatic activity was possibly related to (hydro)fracturing rather than to a magmatic intrusion. If a fresh magmatic intrusion was emplaced, it must have occurred within a restricted zone underneath the lake area (Martínez et al. 2000), since no drastic increases in fumarole temperatures around the dome were observed since late 1988 (Fig. 5).

A new lake started to form in mid August-September 1994 when the peak of the rainy season was near, but it remained shallow and grey due to the vigor of subaqueous fumarolic degassing (Fig. 3) despite the relatively heavy rainfall and the lowering of fumarolic output and temperature (92 °C; Barquero 1998; Venzke et al. 2002). Between October 1994 and January 1995 the lake depth approached ~15–20 m, and in April 1995 it appeared quiet with its typical milky turquoise color (Barquero 1998; Martínez et al. 2000; Venzke et al. 2002).

The limited data available for 1994–1995 showed that PTs returned in significant amounts, apparently due to considerable input of volatiles. Large fluctuations in their concentrations reflect strong variations in gas fluxes. The high PT

concentrations, particularly between September 1994 and March 1995 (except for November 1994 when they were not detected), were marked by a dominance of the tetrathionate ion: $S_4O_6^{2-} > S_5O_6^{2-} > S_6O_6^{2-}$ (Table 1; Fig. 4). These observations suggest that the SO_2/H_2S ratio of the subaqueous fumaroles still remained relatively high. After March 1995 and around the transition between Stage III and Stage IV, input of volatiles and heat seemed to have reduced substantially, as indicated by the sharp decrease in PTs, which coincided with decreasing temperature, acidity, and solute concentrations.

3.2.3 Stage IV (September 1995– February 2005: Relative Quiescence in the Lake, Significant Fluctuations in PT Concentrations and Subaqueous Input of Volatiles and Heat

The three main PTs were present in the lake throughout most of Stage IV, though with variable concentrations (Fig. 6; Table 1). Totals ranged between below the detection limit and 1,640 mg/kg, suggesting drastic changes in the subaqueous fumarolic input. Despite this variability, overall trends shown by the individual species were largely parallel. The tetrathionate ion dominated their distribution ($S_4O_6^{2-} > S_5O_6^{2-} > S_6O_6^{2-}$), except for some brief intervals when pentathionate prevailed ($S_5O_6^{2-} > S_4O_6^{2-} > S_6O_6^{2-}$) and total PT concentrations dropped, as happened in January 1996 and January–April 2002. The unusual distribution of penta-and hexa-thionate dominance over tetrathionate dominance ($S_5O_6^{2-} > S_6O_6^{2-} > S_4O_6^{2-}$) in a few samples collected in November 1984 and January–February 2002 might be due to analytical error or to degradation, since these samples originally contained low amounts of PTs (cf. Takano and Watanuki 1988). The general predominance of the tetrathionate ion throughout Stage IV suggests that the subaqueous fumaroles were relatively rich in SO_2, with a SO_2/H_2S ratio of >0.07 during most the time (cf., Fig. 7).

During Stage IV the total influx of heat and volatiles into the lake was lower than in Stages I–III and V, although in early 2005 strong subaqueous fumarolic activity within the lake turned it into a convective grey and hotter lake. Sites of fumarolic degassing included more sub-aerial vents outside the lake area, extending from the dome to the crater floor and inner crater walls. These conditions may explain the general relative quiescence of the lake during most of this stage, but field observations and the lake chemical and physical properties suggested that it continued to receive a significant input of heat and volatiles during most of Stage IV. The marked fluctuations in PT patterns apparently reflect dynamic changes in activity of subaqueous vents throughout this period. Based on the mode of these variations in PTs and in other monitored parameters, five sub-stages can be distinguished (Fig. 6). Their most salient features are described in the following sections.

Sub-stage IVA (September 1995–July 1997): Relative Quiescence, Large Production of PTs with Predominance of Tetrathionate Due to Renewed Input of Gases, Enhanced Fumarolic Output Through the Dome and Other on-Shore Locations

Following the last months of Stage III when PTs concentrations were high, the transition towards this sub-stage showed first a rapid decline to values near or below detection limits. A concomitant decrease in temperature from 42 to 26 °C, increase in pH from ∼0.7 to 1.6, and shifts towards lower $S_4O_6^{2-}/S_5O_6^{2-}$ and $S_4O_6^{2-}/S_6O_6^{2-}$ ratios (Figs. 3, 5 and 6) argue against thermal breakdown or sulfitolysis of PTs in response to increased subaqueous input of heat and volatiles (cf. Takano et al. 1994b). These observations are instead consistent with a weakening of the injection rate and lower SO_2/H_2S ratios of fumarolic gases, which is further supported by decreasing sulfate, chloride and fluoride concentrations (Fig. 6). Field observations supported this interpretation. After the new lake started to form in mid-August–September 1994, the filling rate was initially slow and the color grey, despite heavy seasonal rainfall (Fig. 3), due to still persistent vigorous fumarolic degassing in

the lake area (Barquero 1998; Venzke et al. 2002). However, after the lake approached ~20 m depth between October 1994 and January 1995, subaqueous fumarolic activity was weak around April 1995 when the lake was fairly quiet with a typical milky turquoise color (Barquero 1998). This quiescence resulted in a rapid and steady increase of the lake volume from May 1995 until 1996, which continued to grow until reaching a record level in November 1997 (Fig. 3). All of these features strongly suggest that the decline in PT levels was caused by a substantial decrease in the input of heat and volatiles that might be caused by temporal partial blockage of subaqueous vents.

Polythionates reappeared in January 1996, after which significant amounts were produced in the course of this sub-stage. Tetrathionate was the predominant species except during the initial build-up when pentathionate briefly prevailed, possibly due to relatively low SO_2/H_2S ratios of subaqueous fumaroles. The rise of concentrations in early 1996 points to renewal of fumarolic input and the large production of PTs towards the end of substage IVA suggests a sustained influx of gases with moderately high SO_2/H_2S ratios (Fig. 7) (cf. Takano 1987; Takano and Watanuki 1990). Although concentrations of the major anions, pH and lake temperature responded to the initial increase in gas flux, a clear correlation was obscured by dilution effects from the steady increase of the lake volume throughout 1995–1997, partly due to above-average rainfall in 1995–1997 (Fig. 3). Hence, in September–December 1997 the lake reached a record level of more than 1.7×10^6 m^3 and a depth of about 45 m (Martínez et al. 2000).

The renewed PT production coincided with enhanced fumarolic activity at the dome and other on-shore locations, and with visible upwelling in the lake. More vigorous fumaroles around the dome started in September 1995, marking the beginning of Stage IV after a 7-year period of only very weak fumarolic activity around the dome (OVSICORI 1995). Fumaroles with temperatures of ~93 °C escaped from old and new fractures located mostly on its northern face above the lake's surface, increasing the

plume height from about 100 m to an average of ~500 m until May 1996. Other features observed at the dome were small flows of molten sulfur, indicating minimum temperatures of 113–119 °C (Shriver and Atkins 1999), minor landslides towards the lake and a constant bubbling below the lake surface near the dome, which persisted until the end of 2001. A small phreatic explosion at the northern face of the dome on 8 April 1996 turned the color of the lake from turquoise to grayish for almost six weeks (OVSICORI 1996). It possibly marked the clearance of fumarolic vents, which were clogged by sediments and solidified sulfur, gypsum and other hydrothermal minerals that accumulated since the previous phreatic periods between 1987 and 1994. Moreover, between 1995–1996, an increase in the amount of soil diffuse CO_2 gas from 0.01 to 2.1% and a shift in the $\delta^{13}C$ values from −21.1 to −6.2‰ measured at the dome (Williams-Jones et al. 2000) indicated a larger permeability, consistent with the more vigorous fumarolic degassing and the occurrence of minor landslides around the dome. The dome remained one of the main sites of fumarolic degassing since then, although degassing rates were variable throughout Stages IV and V.

Elsewhere near the lake shores, initially in the southern sector, later also in the western and north-western sectors, new sub-aerial fumaroles giving off minor columns of vapor and gases (plume heights <100 m, temperatures <97 °C), started manifesting as well (the first sub-aerial fumaroles opened by April 1995). The opening of sub-aerial vents coincided with enhanced A-, AB- and B-type seismicity in 1995 (Fig. 6). They remained active for about 5 years until they ceased completely in June 2000 (Venzke et al. 2002; Mora and Ramírez 2004; Martínez 2008).

During the months immediately before the reappearance of the PTs a remarkable increase in volcanic tremor was registered (on the order of several hundreds of hours per month in October–December 1995), as well as a significant increase in AB and B-type seismicity (Fig. 5). This upsurge in seismic activity was possibly related to build up of pressure in the magmatic-hydrothermal system, opening of cracks or

conduits and movement of fluids (McNutt 2000). Another notable observation is the sharp ~75% drop in B-type seismic events to a level similar to that observed before 1985–1986 (Fernández 1990), after the re-appearance of strong fumarolic activity on the dome in late 1995—early 1996. Thus, sub-stage IVA was marked by a low number of B-type events, which were thought to reflect a lower degree of interaction between the subsurface heat source and the shallow aquifer beneath the crater (Barboza V. pers. comm. 2005). This agrees with the decrease of the lake temperature and anion concentrations, the rise in pH and lake volume, and with enhanced sub-aerial fumarolic manifestations around the dome and onshore locations around the acid lake observed between late 1995 and early 1996.

Sub-stage IVB (August 1997–October 2001): Relative Quiescence But Largest PT Concentrations of the 1980–2006 Period Due to Influx of S-Rich Fumarolic Gas, Predominance of Tetrathionate

From mid-1997 on, PT concentrations first increased until reaching peak levels in early 1998, and then showed sharp drops in April (below detection limits) and June 1998 (Table 1; Fig. 6). This brief interval of low concentrations ended with a rise to values similar to those observed before April. It occurred right after maxima in the $S_4O_6^{2-}/S_5O_6^{2-}$ and $S_4O_6^{2-}/S_6O_6^{2-}$ ratios (Fig. 6), which can be attributed to influx of volatiles with increased SO_2/H_2S ratios or higher flux rates (Takano and Watanuki 1990). The combined trends can be interpreted to result from the continuous injection of gas carrying increasing amounts of SO_2. First a SO_2/H_2S ratio was reached that favored an optimum production of total PTs, then further increased ratios resulted in a more efficient production of tetrathionate compared to the longer PTs (Takano et al. 1994b, 2001), while an excess of unreacted SO_2 finally caused a temporary breakdown of PTs due to sulfitolysis. A subsequent shift back to lower SO_2/H_2S ratios then allowed their formation (Figs. 6 and 7). The inferred increasing volatile input at the beginning of sub-stage IVB is supported by the increasing trend of sulfate, chloride, and fluoride concentrations in the lake (Fig. 6), accompanied by a drop in the pH, while relatively high levels of these anions confirmed that it received a significant influx throughout this sub-stage. Hence, the brief disappearance of PTs in April 1998 was probably the result of their breakdown by sulfitolysis. It is important to note that this absence was not followed by phreatic activity, unlike what happened in March–June 1987 and most the Stage III (Fig. 5).

From November 1998 to October 2001 the PT concentrations showed a steady decline, coinciding with a period when many new fumarolic vents opened, especially along the southern, western and eastern inner crater walls. A brief sharp increase in the concentrations of PTs, $S_4O_6^{2-}/S_5O_6^{2-}$ and $S_4O_6^{2-}/S_6O_6^{2-}$ ratios, major anions, and temperature in September–October 2001, just before the PTs dropped down to below detection limits in November, pointed to a sudden short-lived influx of SO_2-rich fumarolic gases into the lake. This is consistent with peaks in unreacted dissolved SO_2 in the lake, which showed up to 300 ppm in 1999 and up to 255 ppm in the second half of 2001 (Fig. 6).

From August 1997 on, when the lake composition started showing a remarkable change, the concentration of chloride was practically always higher than that of sulfate (except for the interval November 2001–April 2002), pointing to the input of chlorine-rich magmatic gas into the lake, whereas from July 2004 the concentrations of sulfate resulted to be higher than those of chloride (Table 1; Fig. 6). The lake level dropped by about 8 m during the first half of 1998, and remained more or less constant throughout the next two and a half years, despite the significant amount of rainfall in 1999 and 2000, which ultimately led to a lake-level rise in the first months of 2001 (Fig. 3). In Fig. 9 an aerial view of Laguna Caliente with a vapor-rich plume rising from the dome is shown.

Apart from the apparent relationships between PT behavior, lake chemistry and supply of volatiles during sub-stage IVB, there were also a number of noticeable results from various

geophysical signals and surface manifestations monitored during this interval as pointed in the Supplementary data found at http://www.ovsicori. una.ac.cr/index.php/vulcanologia/geoquimica/ investigacion-geoquimica.

Sub-stage IVC (November 2001–May 2002): Relative Quiescence, Sharp Drop in PT Concentrations with Predominance of Pentathionate, Fairly Low Influx of Volatiles

A sharp decline in PTs concentrations to below detection limits characterized this short interval during which the lake activity was relatively calm and visible upwelling ceased. Only very low amounts of PTs were sporadically detected in November 2001–May 2002, with a distribution that was dominated by pentathionate.

The $S_4O_6^{2-}/S_5O_6^{2-}$ and $S_4O_6^{2-}/S_6O_6^{2-}$ ratios were occasionally lower than in the previous years (Fig. 6), suggesting that during this sub-stage the subaqueous fumaroles were significantly depleted in SO_2. Thus, the SO_2/H_2S ratios of the subaqueous fumarolic input shifted from SO_2-excess (unreacted) (>0.07) to H_2S-excess (Takano et al. 1994b) (Fig. 7).

The drop in PT concentrations coincided with a sharp decrease in the concentrations of other major anions, a significant increase in pH and a gradual cooling of the lake water (Fig. 6). Free dissolved SO_2 or H_2S gases were not detected. In addition, the lake color changed from milky turquoise to unusual milky dark bluish, suggesting the presence of less suspended particulate
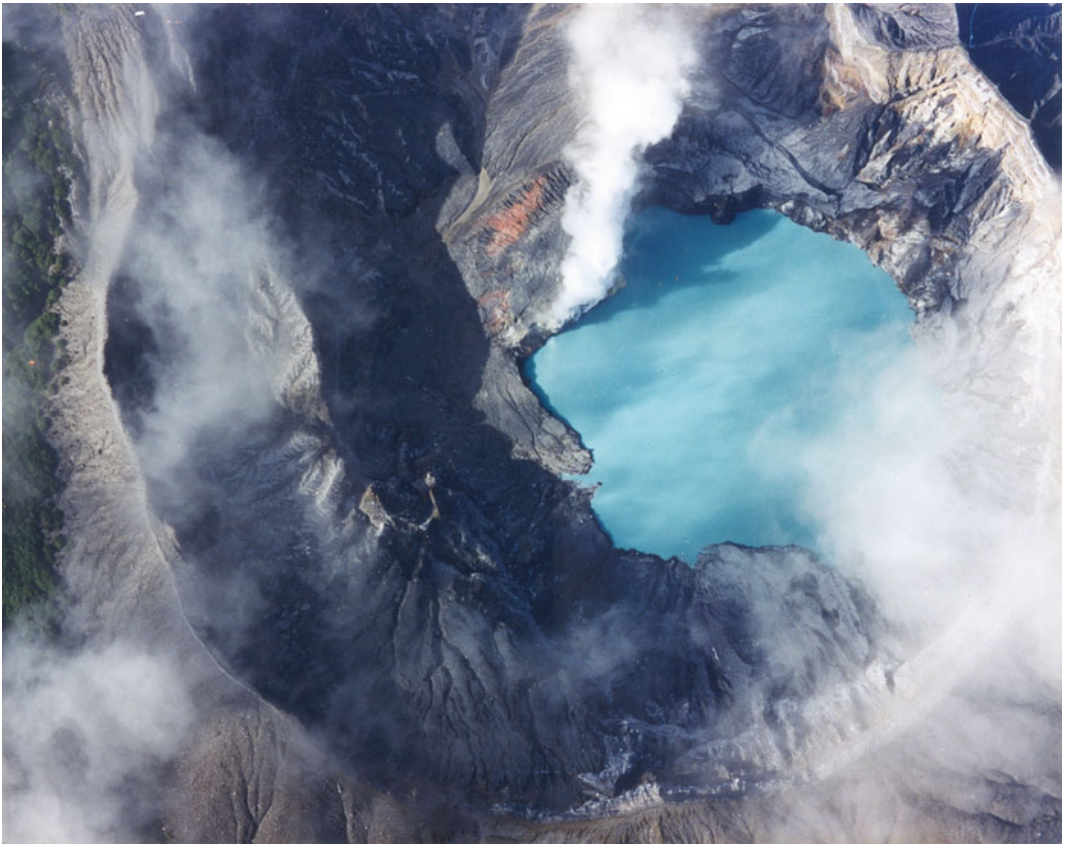
Fig. 9 Aerial view of the active crater of Poás volcano (~1.3 km diameter along its E–W axis). The vapor-rich plume rising from the dome, located on the southern shore of the lake (with its typical blue turquoise color), is related to fumaroles with temperatures around 90–100 °C. Photograph taken from an aircraft by Federico Chavarría Kopper in mid-1999

matter in the water column and much less sub-aqueous fumarolic activity.

Because the lake level volume rather decreased by about 8% between January–June 2002 (Fig. 3), it is clear that these drastic changes can be attributed to dilution of the lake waters, signaling a substantial decrease in heat and volatile supply, presumably because of temporary blockage of the subaqueous fumarolic vents. Hence, the gas output through the lake area was too weak to produce appreciable amounts of PTs.

At the same time, fumarolic activity around the dome abruptly decreased and only a very weak plume of ~ 50 m or less was observed, although vigorous activity continued in the fumarolic field on the eastern side of the crater (Fig. 10). Noticeable decreases in B and AB-type seismic events and absence of high-frequency earthquakes and volcanic tremor were recorded as well (Fig. 5). All these observations point to a significant decrease in the influx of volatiles and heat into the lake.

Sub-stage IVD (June 2002–September 2003): Relative Quiescence, Enhanced Input of Volatiles and Heat, Reappearance of Significant Amounts of PTs, Dominance of Tetrathionate

This sub-stage was marked by renewed heating of the lake and the reappearance of PTs in such amounts that concentrations similar to those observed in 1997–1998 were reached. Overall increasing trends of PT concentrations as well as $S_4O_6^{2-}/S_5O_6^{2-}$ and $S_4O_6^{2-}/S_6O_6^{2-}$ ratios

Fig. 10 View of the active crater from the lookout point (El Mirador) at the southern rim, just a few hours after renewal of phreatic activity some time between the evening of 23 March and the morning of 24 March 2006. Note the gray color of the lake and the dense whitish columns of vapor and gases issued vigorously and simultaneously from the lake surface and from the Fumarole Norte near the NE edge of the lake. Rock fragments and sediment lumps on the flat crater floor were ejected from the lake. Photograph taken by Dr. Geerke Floor on 24 March 2006 around 3:30 p.m.

coincided with substantial increases in the lake-water temperatures (from 29 to 41 °C) and SO_4, Cl and F concentrations, and with a concomitant decrease of pH (Fig. 6). It is noteworthy that temperature and PT concentrations showed parallel trends with peaks around September 2002 and June 2003, whereas those of SO_4^{2-}, Cl^- and F^- continued to accumulate until July–September 2003. This period of high PT concentrations terminated by a sudden decline to below detection limits in October 2003.

Dominance of tetrathionate throughout the sub-stage and presence of unreacted dissolved SO_2 in the lake water point to relatively high SO_2/H_2S ratios of subaqueous fumaroles. The patterns of the individual PTs fluctuated and were not always parallel, especially during the second half of this interval (Fig. 6), suggesting variations in the injection rates and proportions of SO_2 and H_2S.

It is of interest to note that during this sub-stage the PT concentrations did not follow the steadily increasing trends of SO_4^{2-}, Cl^- and F^-, but showed peaks that rather tended to correspond with peaks in the lake temperature (Fig. 6). The decrease of PT concentrations when major anions still continued to rise may be the result of sulfitolytic breakdown or reflect an influx of (recycled?) brine water into the lake. The latter alternative would be supported by the corresponding early decrease of the temperature and by a gradual increase in the Cl^-/F^- and Cl^-/SO_4^{2-} ratios, which were observed in the second half of this sub-stage. This might also fit with an overall pattern of increasing importance of Cl^- relative to the other anions observed throughout Stage IV (Fig. 6).

Simultaneous with the return of PTs, the appearance of the lake changed significantly. In late May-early June 2002, it recovered its typical milky sky-blue color after the previous months when it was milky dark blue, apparently due to the small load of suspended particles. In late July 2002 the lake turned dark greenish due to convective circulation that transported abundant sulfur globules and bottom sediment to the surface in the central part of Laguna Caliente.

Convection and floating sulfur globules were observed practically throughout the entire sub-stage, but the activity was particularly strong in September–October 2003 when some small unusual blackish globules appeared together with the commonly observed yellow sulfur globules and fragments of molten sulfur with a 'soft elastomeric' texture emerged from the lake bottom, suggesting an intensification of subaqueous fumarolic output (cf. Takano et al. 1994a). At the same time, especially between September 2002 and December 2003, a persistent emanation of acidic fumes (HCl evaporation?) formed a white acidic fog over the lake, which covered at times the entire surface. Constant bubbling was observed at the interface between the lake and the north face of the dome, where water "spurts" of about 1–5 m length were sporadically ejected between August 2002 and September 2003. In spite of the large and relatively constant volume ($\sim 1.5 \times 10^6$ m^3), the lake level showed some fluctuations, possibly as a result of lower yearly rainfall in 2002 (Fig. 3) in combination with stronger evaporation in 2002–2003 due to the increased input of heat.

Throughout this sub-stage, the fumarolic emissions from the dome remained modest and fairly constant, producing a less than 400 m high plume, except for a short-lived increase up to 600 m in February 2003. New thermal springs, fumaroles and cracks continued to appear in the eastern sector of the crater, and their plumes reached heights between 50 and 300 m similar to the previous sub-stage. In December 2002, the temperature of the Fumarola Norte rose from boiling point to 122 °C (Fig. 5). Bright reddish-orange and white hydro-sulfosalts were observed along the Norte-Este and Este and acid sulfate-rich springs in the eastern side of the crater. In early January 2003, an OVSICORI field survey provided indications about a minor hydrothermal explosion, which occurred within the area where the Este springs seeped out in the previous month. The concentric cracks that appeared along the eastern inner terrace in July 1999 became wider, and crater wall collapses were observed. All these manifestations thus indicate that, during this period, the release of

fumarolic gas was concentrated in an area comprising the dome, the lake and the eastern inner crater wall.

Following a substantial drop in the number of events recorded by the end of the previous interval, B-type and AB-type seismic activity increased during this sub-stage, reaching maximum intensity between September–October 2002. The increase accompanied the appearance of new fumaroles on the dome and in the eastern sector of the crater. At the end of the sub-stage, AB-type seismicity decreased substantially, whereas B-type earthquakes continued to be recorded in large quantities.

Rare types of short-duration monochromatic tremors, which are distinct from the continuous long-duration tremors typically recorded at Poás, as well as "banded" tremors (a rarity for this volcano) and "intrusive" signals were registered by the OVSICORI POA2 seismic station between mid-2002 and the end of 2003. Short-duration (<1 min) monochromatic tremors and "intrusive" signals were also recorded in 1986 before renewal of geyser-like phreatic activity in the crater lake, and related to the ascent of minor magmatic intrusions (Fernández 1990; Rowe et al. 1992a).

Microgravity surveys showed a rise in sub-surface mass at stations to the west and south of the dome between 2000 and 2009, which was attributed to a highly localized dendritic intrusion beneath the crater (Rymer et al. 2005, 2009), similar to other inferred events associated with microgravity rises over the last 20 years (Fig. 5). The enhanced input of heat and SO_2-rich volatiles into the lake system, in combination with the accompanying manifestations, might be consistent with an ongoing minor intrusion of magma during sub-stage IVD, but without triggering phreatic explosions.

Sub-stage IVE (October 2003–February 2005: Relative Quiescence, Sharp Drop in PT Concentrations, Strong Weakening of Fumarolic Outgassing, Record Lake Level)

A sharp decline in PT concentrations to below detection limits in October–November 2003, comparable to that observed in sub-stage IVC, was the start of this period of quiescence, which was marked by much less input of heat and volatiles into the lake. Polythionates were monitored and remained undetected until April 2005. In the few determinations conducted during this period, only traces of dissolved SO_2 and no H_2S were detected between June 2004 and March 2005. The lake temperature, which had decreased gradually from a maximum of 41 °C in April–June 2003, ranged between 23 and 35 °C during the second half of 2003 and throughout 2004. Anion concentrations decreased substantially, with fluoride showing the lowest values ever measured at Poás, which were related to the very high SO_4^{2-}/F^- and Cl^-/F^- ratios observed in May–June 2004. The pH increased by about 0.7 units meaning that the lake was about 5 times less acidic (Fig. 6).

From late 2003 on, the lake volume increased significantly and continued growing until at least 1.9 million m^3 between late 2004 and early 2005, reaching the highest volume recorded since the late 70s and culminating in the flooding of part of the eastern crater floor. Sub-aerial fumaroles in this sector remained submerged for several weeks (OVSICORI 2005). This expansion of the lake was caused by extremely heavy rainfall in the wet seasons of 2003, 2004 and 2005 (Fig. 3), which were among the rainiest years recorded at the summit of Poás volcano in the last 15 years (ICE rainfall data; Aguilar et al. 2005). The volume increase was accompanied first by a subtle color change towards the end of 2003, but at the end of April 2004 it turned from bluish green to emerald green (see photos at the Supplementary data to this article available online at http://www.ovsicori.una.ac.cr/index.php/vulcanologia/geoquimica/investigacion-geoquimica). After decades of monitoring, this was the only time that such a color was seen (Martínez 2008). A similar color was also observed in other acid crater lakes during periods of reduced gas emission (e.g. White Island, Venzke et al. 2002).

A conspicuous reduction in the vigor of fumarolic outgassing was observed around the dome, which was one of the main sites with persistent strong gas and vapor emission since late 1995. The plume that typically reached a height of 500 m or more remained particularly

low (<200 m) throughout most of 2004, occasionally allowing to observe some of the vents. Outlet temperatures of fumaroles on the dome remained rather constant, i.e. around boiling point at the altitude of the crater (93 °C). In contrast, vigorous sub-aerial fumaroles (up to 120 °C) continued in the eastern fumarolic field. The Fumarole Norte (Figs. 5 and 10) showed a temperature rise up to 116 °C, and some new fumaroles opened, which is consistent with the recorded high number of B and AB-type earthquakes during this sub-stage (Fig. 5). During the peak of the dry season of 2005 (March–April), deposition of bright yellow-orange insoluble or readily soluble acid alteration minerals such as hydroxysulfates (e.g. alunite, alunogen, jarosite), and some water-soluble hydroxysulfates (mohrite, pickeringite, dietrichite, kaolinite, halotrichite, apjohnite, voltaite, bilinite, römerite), were once again observed along the Norte-Este and Este acid sulfate-rich springs (Martínez 2008; Rodríguez and van Bergen 2015, 2017). Landslides continued to accompany the vigorous fumarolic activity in this sector.

The large decrease in the flux of fumarolic gases and heat within the area between the lake and the dome might be the consequence of a structural change which led to a localized blockage of the gas conduits beneath the lake, without affecting the fumarolic field in the eastern region that started forming in late 1998 and 1999. Another cause of the weakening fumarolic input into the lake to be considered is a stronger gas scrubbing (Symonds et al. 2001) due to an increased amount of groundwater table, in agreement with a significant rise of the lake water level between mid-2003 and early 2005.

3.2.4 Stage V (From March 2005 to February 2019): Reappearance of Large Quantities of PTs, Dominance of Tetrathionate, Subsequent PT Breakdown at Onset of the Current Cycle of Phreatomagmatic to Magmatic Activity

This period is marked by peak activity, culminating in phreatic explosions in March, April,

September and December 2006, and includes the most recent PT data available (Table 1). After their absence for more than a year, the PTs reappeared in April–May 2005, after which their abundance increased sharply until reaching maximum total concentrations of about 3,500 mg/kg between November 2005 and January 2006 (Figs. 3 and 6). Subsequently, between April–May 2006 shortly after the onset of phreatic activity in March, a steep decrease was observed down to values of 150–620 mg/kg. Excess (un-reacted) dissolved SO_2 was detected in the lake water between May 2005 and late 2006, and the order of species abundance was virtually always $S_4O_6^{2-} > S_5O_6^{2-} > S_6O_6^{2-}$, indicating that the injected gas was again characterized by a relatively high SO_2/H_2S ratio. An exception was observed in May–July 2006 when pentathionate was dominant, coinciding with the presence of ca. 2 mg/L of dissolved H_2S in July, the first time that this species was detected since 1999. The $S_4O_6^{2-}/S_6O_6^{2-}$ ratios at the onset of Stage V were the highest recorded in 25 years, while the $S_4O_6^{2-}/S_5O_6^{2-}$ ratios were close to stage IV values (Figs. 4 and 6). Tetra- and pentathionate showed fluctuating but parallel trends, whereas hexathionate was initially produced in very small amounts and gradually increased in the course of 2005-early 2006. The strong decrease of PTs that started in late 2005-early 2006 and their low concentrations in 2006 are apparently due to sulfitolytic (and thermal?) breakdown caused by a sustained influx of SO_2-rich gases, since the decline occurred during a period of steadily increasing SO_4–Cl–F concentrations and temperature as well as decreasing pH (Fig. 6). Starting from 22 °C in February 2005, the lake temperature rose sharply in the next months until reaching peaks of 50–54 °C in the second half of 2005 (Fig. 6), similar to temperatures registered during the latest period of phreatic eruptions in 1994.

The intensification of activity was accompanied by marked changes in the appearance of the lake. It turned from a calm green reservoir in 2004 to a grey fuming lake in early 2005 (Fig. 10), showing several convective cells that

brought up abundant dark gray and large (∼0.5 cm diameter) sulfur globules. The lake level dropped several meters throughout 2005 despite of heavy rainfall at the summit of the volcano in 2004 and 2005 (Fig. 3). Strong evaporation of acidic fumes affected the sparse vegetation within the crater.

All these observations pointed to a significant new influx of condensing magmatic gases and heat that affected the entire lake system. From early 2005 on, the combined changes in geochemical and seismic behavior could be interpreted as precursory signals to pending phreatic outbreaks, presumably associated with new gas releases provoked by either fracturing of the brittle envelope of a cooling magma body or the intrusion of a fresh magma batch. The latter alternative is supported by increases in micro-gravity in the south-western part of the crater floor since 2001 (Rymer et al. 2004, 2005, 2009), which would imply that magma emplacement at shallow levels started already about halfway Stage IV (Fig. 5).

In early 2006, further changes in monitored signals, pointing to a continued increase in the input of hot gases into the lake and conduits of sub-aerial fumaroles, were the prelude of phreatic eruptions that took place in March, after a period of almost 12 years of relative quiescence. Several mild phreatic eruptions from the lake were observed in March–April 2006. Later that year, at least two small phreatic eruptions occurred on 25–26 September and a visitor of Poás Volcano National Park reported another (about 30–50 m high) on 16 December.

It is conceivable that deep penetration of large amounts of meteoric groundwater into the magmatic/hydrothermal system played a role in triggering the phreatic activity, given the high record of rainfall registered between 2003 and 2005, the flooding of the eastern crater floor and the rate of degassing, fracturing and wall collapses in the eastern sector (cf. Vaselli et al. 2003 and Section on Substage IVB in this paper for a similar mechanism to explain the expanding fumarolic activity in 1998–2000). However, the strong rise in all magmatic volatiles, particularly SO_2 and HF, argues for new releases from a magma source as main controlling factor.

A possible connection between subaqueous and sub-aerial fumarolic degassing will be discussed below.

During Stage V, fumarolic degassing was centered within the lake area and the fumarolic field in the eastern sector. The Fumarola Norte at the NE inner crater wall (Fig. 10) showed sudden changes in temperature (from 105 °C in March 2005 to 200 °C in May 2005), as well as changes in gas composition, especially between May 2005 and early 2006. It released large amounts of sulfur crystals that were deposited over a large area of the northeastern inner crater wall, and molten sulfur ponds formed in the vents and flowed towards the vicinity of the acid lake. Emissions from the dome remained moderately low at <95 °C, similar to the previous stage (Fig. 5).

In April 2006, shortly after the climax of renewal of phreatic activity, an average SO_2 flux of approximately 100 tons/day was recorded by mobile Mini-DOAS (OVSICORI 2006; Barrancos et al. 2008). This flux did not reach the Stage-II levels of 500–800 tons/day measured in 1981–1983 (pers. comm. Stoiber, cited in Prosser and Carr 1987; Casadevall et al. 1984b; Stoiber et al. 1986) but was higher than the 29 tons/day in March 2003 and similar to the 90 tons/day measured in early 1991 (Andres et al. 1992).

The onset of increased activity in the lake coincided with a strong increase in seismicity between April and November 2005, particularly AB-type events and polychromatic as well as monochromatic tremors. This was only the second time that such an exceptional amount of volcanic tremor was recorded at Poás since the period of peak heating in 1981–1983 (Stage II), which was presumably due to a magmatic intrusion beneath the dome (Brown et al. 1991) where fumaroles reached temperatures of more than 1,000 °C (Fig. 5). Moreover, it was the first time for AB-type events to reach such a high record, but it is unknown if they were similarly abundant in Stage II because they were not classified as such before 1984. Clear increases in AB-type quakes and polychromatic tremor preceded and accompanied the different intervals of phreatic eruptions in 2006 (Fig. 5). Swarms of A-type quakes were registered in January–

February, April and June–July 2005, but their number remained relatively modest compared to other periods with increased seismicity of this type.

By the end of 2006, dissolved volatiles in the lake reached the highest levels of Stage V. Highest temperatures were recorded in November (58 °C) after a minor dip in the previous months. The lake retained its grey color and continued to show strong convective activity. A few minor phreatic explosions, "mud plumes" and molten sulfur floating on the surface further characterized its behaviour until 2008. Between 2009 and 2017, there were numerous phreatic explosions with jetting columns up to m high and fumaroles which temperature ranged from above 100 °C (in 2008–2009) to around 625 °C (in 2011 and 2015, and ca. 1000 °C (in 2017) (Vaselli et al. Chapter "The Last Eighteen Years (1998–2014) of Fumarolic Degassing at the Poás Volcano (Costa Rica) and Renewal Activity"). Stage V reached a peak activity in April–June 2017, with phreatomagmatic and magmatic eruptions. From then on, the volcano is showing subaerial degassing and frequent weak phreactic eruptions impacting the ambient around, mainly downwind.

3.3 Lake Behavior from Polythionate —Sulfate Relationships

Polythionate concentrations in the Poás lake have rapidly declined several times over the 1980–2006 period. These events are not obviously related to corresponding increases in sulfate concentrations (Figs. 4 and 6) because it can be inferred that different mechanisms, associated with either increased or decreased activity, have played a role.

The PT decrease at the start of the active Stage III was accompanied by an increase in the sulfate concentrations, pointing to sulfitolysis and/or thermal breakdown. This can only account for about 16% of the increase in sulfate observed between May and July 1986 (Fig. 4). Hence, increased input of hot SO_2-rich volatiles was likely responsible for most of the sulfate production, consistent with an increase in the SO_2/H_2S

ratio of subaqueous fumaroles, as inferred from the change in the distribution of PT species since August 1986 (Fig. 4) (albeit with temporary reversals in some of the late 1986 and early 1987 samples). On the other hand, PT decay may account for the sulfate increase of March–April 1998 (Sub-stage IVB), and November 2005–May 2006 (Stage V). It is of interest to note that precipitation of gypsum/anhydrite, barite, celestite, aluminium-hydroxysulfate minerals, and native sulfur may obscure the inverse relation between dissolved sulfate ions and PT decomposition, since the lake water is usually saturated or nearly saturated with respect to these sulfate mineral phases (Rodríguez 2016).

The three other intervals in Stage IV with a short-lived decline in PTs (Fig. 6) require a different explanation. Decreased SO_4^{2-}, Cl^-, F^- and dissolved SO_2 concentrations, increased pH and a drop in temperature during these periods point to a reduction or complete cessation of subaqueous fumarolic venting. Marked peaks in SO_4^{2-}/F^- and Cl^-/F^- ratios reflect a stronger decline of F relative to the other anions, which is consistent with less magmatic input, given the preferential reaction of HF with wall-rocks at relative low temperatures of volcanic gases (cf. Symonds et al. 1990; Stimac et al. 2003). The observations thus provide evidence for temporary clogging of subaqueous fumarolic vents and a decrease in the heat flux. A parallel short-lived decrease in SO_2/H_2S ratios of subaqueous and sub-aerial fumaroles during Sub-stage IVC suggests that this blockage affected large parts of the subsurface system feeding the entire crater area. During Sub-stage IVE, however, lower SO_2/H_2S ratios were only observed in the lake water, while sub-aerial fumaroles showed a subtle systematic change.

Furthermore, the cessation of convective activity would promote the development of stratification in the water column, including an aerated shallow layer. According to experiments on Yugama lake water, PT concentrations are relatively insensitive to aeration (Takano and Watanuki 1990), but the combination of oxygen and Fe^{3+} at low pH oxidizes PTs to sulfate to an

order of magnitude faster than oxygen alone (Druschel et al. 2003). A representative reaction describing this oxidative decomposition (cf. Takano and Watanuki 1988; Takano et al. 2001; Druschel et al. 2003) is, as follows:

$$S_4O_6^{2-}{}_{(aq)} + 3Fe^{3+}{}_{(aq)} + 2.75\,O_{2(aq)}$$
$$+ 4.5\,H_2O_{(l)} \rightleftharpoons 4\,SO_4^{2-}{}_{(aq)} + 3\,Fe^{2+}{}_{(aq)} + 9\,H^+{}_{(aq)}$$

(d)
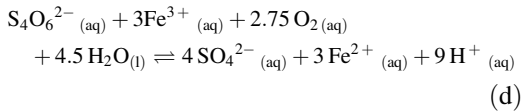
Because an influx of oxygen-rich fresh rainwater into the lake will promote the oxidation of Fe^{2+} into Fe^{3+}, and because low Fe^{2+}/Fe_{Total} ratios (~ 0.01) were indeed found by us in samples of surface water during periods with stagnant fumarolic input (unpublished data), it is conceivable that this mechanism has further enhanced the PT breakdown.

Finally, microbial decomposition of PTs may also have contributed to their disappearance at the start of Sub-stage IVA and during Sub-stages IVC and IVE when bacterial activity could have been boosted by relatively high pH conditions, as was also observed in the ultra acid crater lake of Maly Semiachik volcano (Takano et al. 1995, 1997). So far, the presence of *Acidithiobacillus* sp. in the lake water of Poás (Sugimori et al. 1995, 2001) and some rod-shaped and spherical acidiphilic bacteria in the bottom sediments has been reported and are likely to be new species (Sugimori et al. 2002). Recently, Hynek et al. 2018, found in the acid lake of Poás bacteria of the genus acidiphilium such as: acidiphilium angustum, acidiphilium rubrum and A. acidophilum (formerly Thiobacillus acidophilus). However, the potential effect of micro-organisms on the PT budgets remains to be assessed.

3.4 SO₂/H₂S Ratios and Common Feeding Controls of Subaqueous and Sub-aerial Fumarolic Output

Molar SO_2/H_2S ratios in the lake brines were estimated from the concentrations of dissolved SO_2 and H_2S gases that are in excess (unreacted)

in the lake waters and that were discontinuously measured in situ since 1999. Since SO_2 is more soluble in water than H_2S, the SO_2/H_2S ratio of gas species dissolved in the lake water will be larger than that of the injected fumarolic gases (e.g. at 20 °C, SO_2 is about 15 times more soluble than H_2S in pure water, Takano et al. 1994b; IUPAC 1983, 1988). Thus, the calculated SO_2/H_2S ratios of subaqueous fumaroles are based on the solubility of both gas species in pure water at 1 atmosphere for the lake temperatures measured (IUPAC 1983, 1988; Xia et al. 1999, 2000), assuming that the solubility values are also valid for the acid and highly saline brines of Poás lake. To estimate the SO_2/H_2S ratios of the subaqueous fumarolic gases a H_2S concentration of 0.2 ppm (detection limit) was adopted, because H_2S was only detected a few times over the period during the surveys of dissolved gases (about 2 ppm in July 2006, May 2009, Sept–Oct 2012, and Oct–Nov 2014). Hence, the calculated ratios reported here (Fig. 6) should be taken as minimum values. Dissolved unreacted SO_2 was always detected in significant amounts, except in November–December 2001 and June 2004–March 2005, when traces were measured at most.

The inferred SO_2/H_2S ratios of subaqueous and sub-aerial fumaroles are similar in magnitude and, with the exception of Sub-stage IVE, show parallel behavior in the time series since 1999 (Fig. 6), which indicates that gas entering at the lake bottom has largely the same source as that emitted from the on-shore vents. The disappearance of PTs coincided with a parallel decrease in the SO_2/H_2S ratios during Sub-stage IVC, whereas in Sub-stage IVE a decrease was only seen in the subaqueous fumaroles, suggesting a decoupling with pathways to the sub-aerial vents during this period. This may imply that in Sub-stage IVE (partial) blockage of rising gases was confined to relatively shallow levels below the lake.

Common feeding controls and gas source for sub-aerial and subaqueous fumaroles are further suggested by field observations. A simultaneous increase in vigor of vapor and gas release from the lake surface, the dome fumaroles and Fumarola Norte was observed in March 2006

(Fig. 10), and both the lake water and the Fumarola Norte showed a simultaneous conspicuous temperature increase in 2005 (Fig. 5). These observations suggest that the fumarolic field on the eastern terrace resulted from fractures going deep below the crater floor (cf. Fournier et al. 2004).

4 Summary

1. According to a 25-years monitoring record, polythionates (tetra-, penta-, and hexathionate), together with other sulfur-bearing species, are commonly present in the acid crater lake of Poás despite wide fluctuations in temperature, chemical composition and volume. Although PTs usually constitute a significant part of the total sulfur budget of the lake, they were only detected as long as the lake temperature did not exceed 60–65 °C and the rate of injection of SO_2 gas were not excessive. In general, large amounts (up to 4,100 mg/kg) were present during periods when strongest fumarolic output occurred sub-aerially and was centered mainly outside the lake area (i.e. Stages II and IV). In contrast, PTs were virtually absent when strong fumarolic activity was predominantly located within the lake area (i.e. Stage III and part of Stage V), thus promoting thermal and sulfitolytic breakdown. Polythionates were also absent during quiescent periods when sub-aqueous fumarolic release was very weak, presumably due to partial sealing of feeding conduits (i.e., early sub-stage IVA, and sub-stages IVC and IVE).

2. The prevailing distribution of PTs is $S_4O_6^{2-} > S_5O_6^{2-} > S_6O_6^{2-}$. This order was predominantly observed in periods when PT concentrations were particularly high, reflecting substantial influx of gas with relatively high SO_2/H_2S ratios into the lake, as was the case during large parts of Stages III, IV and V. Relatively modest concentrations of PTs were usually associated with the sequence $S_5O_6^{2-} > S_4O_6^{2-} > S_6O_6^{2-}$, which is typical for weakened flux rate and/or decreased SO_2/H_2S ratios of gases entering the lake, as observed during Stage II and some short intervals later.

3. The strong fluctuations in PT concentrations and speciation observed over decades reflect the dynamic character of the magmatic-hydrothermal system of Poás. Processes that control the underlying changes in volatile input include shallow intrusions of fresh magma, fracturing of the brittle envelope of cooling magma, and opening, closure or spatial shifts of conduits and fractures that determine the location of fumarolic activity and thus the degree to which volatiles are intercepted by the lake.

4. Polythionates are sensitive signals of renewed input of sulfur-rich gas into the lake, caused by either an intrusion of fresh magma or fracturing of the brittle carapace around cooling magma that was earlier emplaced. An increase in PT concentrations, a change in their speciation from penta- to tetrathionate dominance, possibly followed by a sharp concentration drop caused by sulfitolytic breakdown, likely precede phreatic eruptions several months before the eruptive activity takes place. Intervals during which PT formation was probably associated with such a sequence are early 1984—early 1986 (Stage II–III transition) and early 2005—early 2006 (beginning of Stage V). In both cases, the build-up was accompanied by an increase in temperature and a decrease in pH and volume of the lake. It is noteworthy, however, that a rise of PTs, followed by a drop is not necessarily a prelude to phreatic eruptions, as was illustrated by the disappearance of PTs during Sub-stage IVE following their rise in Sub-stage IVD (mid 2002–mid 2003). Apparently, this episode was marked first by a reduction of sulfur-rich gas input, and then by a virtual cessation of volatile and heat supply, as a temperature drop and pH increase confirmed.

5. The release of sulfur-bearing gas from the magmatic-hydrothermal system can be monitored reliably through time-series analysis of PT species in the lake. This approach is complementary to traditional gas monitoring at sub-aerial fumarolic vents, and has practical advantages in terms of sampling and analytical techniques, except for the non availability of commercial penta- and hexathionate stable salts for the calibration standards. Interoretatuibs will benefit from simultaneous monitoring of other chemical and physical parameters, since our time series demonstrate that changes in the composition and flux of volatiles into the lake, inferred from PTs, are also reflected by changes in other dissolved components and in the level and/or nature of seismic activity.

Supplementary data to this article can be found online at http://www.ovsicori.una. ac.cr/index.php/vulcanologia/geoquimica/ investigacion-geoquimica.

Appendix: Sampling Strategy and Analytical Procedures

Sampling

Samples selected for PT analysis were routinely collected at a location on the NE side of the acidic crater lake (Fig. 1). Temperatures of the lake were measured at the same site using thermocouples. Most of the samples were stored in dark high-density polyethylene bottles at ambient temperature without filtration, dilution or addition of preservatives before the PT analyses were conducted. Between March 1990 and 1995 the sampling intervals were irregular in part because of the high activity of the volcano. From 1996 till November 2006, the data represent a monthly sampling frequency. A single available sample from 1980 was analyzed to record the earliest PT signal. Polythionate data documented by Rowe et al. (1992a) cover the period November 1984–March 1990 and represent an approximate sampling frequency of once every two months. Collectively, the currently available PT record thus covers the period 1980–2006. Some stored samples collected in 1988–1994 that contained grey muddy material were taken from mud pools that were formed during episodes when the lake volume was strongly reduced. These pools had a highly variable chemistry since they were largely mixtures of brine left during evaporation of the lake, fumarolic steam condensing at the bottom of the pools, and rainwater (Rowe 1994). Some pools contained unusual high concentrations of PTs (e.g. $\Sigma S_x O_6^{2-}$ 6,740 mg/kg in a sample of 10 June 1994), but their results are not considered representative for the long-term evolution of the lake system and will therefore be ignored in this study.

Polythionate Analysis

About 190 lake water samples were analyzed for tetra-, penta-, and hexathionate ions at the Department of Chemistry of Tokyo University (Japan) and at the Laboratory of Atmospheric Chemistry (LAQAT) of the Universidad Nacional (Costa Rica) using similar ion-pair chromatographic techniques described below.

At Tokyo University tetra-, penta-, and hexathionate ions were determined following a high-performance microbore ion-pair chromatographic separation technique with ultraviolet absorption detection, and an ion-pair chromatographic separation technique with conductivity detection (Takano 1987; Takano and Watanuki 1988, 1990). The first technique allows the determination of tetra-, penta-, and hexathionate in excess of 0.2 ppm, and the second that of tetra-, and pentathionate in excess of 10 ppm. Standard solutions for penta- and hexathionate were prepared from synthesized salts (Takano and Watanuki 1988) following Goehring and Feldmann (1948). A commercially available potassium tetrathionate salt was re-crystallized for the preparation of tetrathionate standard solutions.

At LAQAT, separation and quantification of main PT species were performed using an ion-pair chromatographic technique with UV absorption detection following Miura and Kawaoi (2000) but using a silica ODS-2 chromatographic column as described below. A Shimadzu Model LC-10AS chromatographic system, equipped with a LC-10AS liquid delivery isocratic pump set at a flow rate of 0.6 mL/min, an automatic SIL-10A auto-injector with a 100 μl sampling loop, a SPD-10AV UV-VIS spectrophotometric detector set at 230 nm, and a SCL-10A system controller were employed. Chromatographic signals were obtained with the following settings: an Alltech/Allsphere ODS-2 analytical column 5 μm particle size (150 × 4.6 mm i.d.) coupled to a Brownlee guard column (50 × 3 mm i.d.); an acetonitrile-water (20:80 v/v) mobile phase (6 mM in tetra-propyl-ammonium hydroxide, TPA, and buffered at a pH = 5.0 by dropwise

addition of glacial acetic acid 100%), filtered through a 0.45 μm membrane filter and degassed by vacuum. All of the reagents used for the mobile phase were analytical-grade; the acetonitrile was 99.93% HPLC grade, the TPA ion pair reagent used was an aqueous solution 20% ($\sim$1 M). Mobile phase, samples and standard solutions were diluted with distilled and deionized water. Samples were filtered and diluted immediately before injection into the chromatographic system. Chromatographic separations were carried out at ambient temperature (23 ± 2 °C).

A potassium tetrathionate calibration solution was injected several times during a 6 h sequence to monitor the response, the reproducibility of peak heights and retention times. Precision of retention times for standards and unknowns was ±0.9% within one day (n = 12) and ±1% within one week (n = 10) for the ion-pair UV chromatographic technique. This enabled unequivocal identification of the PTs by retention time only. Repeated analysis (n = 6) of the 21 June 2002 lake water sample to determine the reproducibility of the procedure yielded a relative standard deviation (RSD) of 5% at a mean concentration of 190 mg/kg for tetrathionate, 4% at 57 mg/kg for pentathionate, and 4% at 25 mg/kg for hexathionate. Reproducibility for the entire set of samples, analyzed in Costa Rica within a three-month period, was tested on randomly selected samples with a range of concentrations. Results showed average RSD values of 10, 7 and 8% for tetra-, penta-, and hexathionate, respectively. All samples were analyzed in duplicate and the results were averaged. Concentration differences between duplicates were usually <5%. Detection limits were 5 mg/kg for tetra-, 1.6 mg/kg for penta-, and 0.5 mg/kg for hexathionate.

One liter of lake water (original T = 32 °C, pH = 1.1, density = 1.02 g/mL), collected on 17 March 1999, was stored at 5 °C and used as a reference standard solution for PT calibration curves at LAQAT. This sample was periodically analyzed at Tokyo University to monitor its quality, in view of the chemical lability of PTs (Stamm et al. 1942). For instance, the analysis

carried out at Tokyo University on 28 July 2002, 3 years and 4 months after collection, yielded 462 ± 8 mg/kg $S_4O_6^{2-}$, 182 ± 3 mg/kg $S_5O_6^{2-}$ and 120 ± 2 mg/kg $S_6O_6^{2-}$, concentrations that were in good agreement with those measured in April 1999 (455, 213 and 110 mg/kg, respectively). Polythionate concentrations in this reference sample remained at acceptable stable levels at least until August–October 2002 when analyses were run at LAQAT.

Some samples were analyzed within a few weeks after collection, but the vast majority was stored for several years at ambient temperature without preservation measures. Although it was demonstrated for natural and synthetic highly acid solutions (pH < 2), free from sulfur-oxidizing bacteria, that no significant decomposition of PTs occurs at concentrations of >100 ppm over at least eight years (Takano 1987; Takano and Watanuki 1988, 1990; Takano et al. 1994), the stability of PTs was verified in some lake water samples at LAQAT. As samples from the 1984–1990 period (Rowe et al. 1992a) were not available for re-analysis, a PT-rich mud pool sample and the reference sample (June 10, 1994 and March 17, 1999), were analyzed for tetrathionate on October 16, 2002 using a fresh synthetic aqueous solution of a 98% sodium tetrathionate dihydrate salt, $Na_2S_4O_6.2H_2O$, to prepare a calibration curve. Results were even somewhat higher than those obtained in Tokyo in 1999 and 2002 (RSD = 14 and 12%), indicating that there is no evidence for significant instability of this species over a period of at least three years. On the same date, all major PTs were also re-analyzed in the 10 June 1994 sample, using the 17 March 1999 reference solution. Original and newly measured values were in reasonable agreement with 2,825 and 3,185 mg/kg for tetra-, 2,067 and 2,600 mg/kg for penta-, and 725 and 880 mg/kg for hexathionate, respectively. Repeated analyses of aliquots of the reference solution in Tokyo in 1999 and 2002 confirmed that it had maintained its quality after three years.

Comparison of concentration data obtained on aliquots of 8 samples (June 1994–September 2001) showed random differences between results from the two laboratories. Overall deviations from the mean values were better than 20% RSD (3–20% for tetra-; 2–15% for penta-, and 1–20% for hexathionate. As most analyses in Tokyo and Costa Rica were carried out with time differences of about 3 years, it is concluded that the PT time series presented here are largely unaffected by potential interlaboratory differences or chemical instability. Re-analysis of sulfate and chloride suggested that some of the oldest samples may have experienced a certain degree of evaporation or mineral precipitation during storage. According to enrichments of both anions found, this may have raised PT concentrations in these cases by 15–20% at most.

Determination of Major Anions, Dissolved Gases, pH and Other Data

Most of the samples collected between 1990 and June 2004 were analyzed for sulfate, chloride and fluoride at Utrecht University by suppressed ion chromatography, using a fully automated Dionex Model DX-120 system. Samples were filtered in the laboratory with 0.45 μm polycarbonate membrane filters prior to analysis. Repeated analysis ($n = 14$) of a lake water sample yielded relative standard deviations better than 4% for all of the anions. Precision was about 0.1, 0.3 and 4% for sulfate, chloride, fluoride, respectively, based on the analysis of a synthetic solution. Detection limits were 0.3, 0.1 and 0.05 mg/kg, respectively. Some samples collected in 2000 were filtered with 0.45 μm polycarbonate filters and diluted in the field to prevent precipitation of gypsum. From comparison with results of samples that were untreated in the field, it was inferred that precipitation of gypsum during storage might have lowered the sulfate concentrations by about 7%. Results of four untreated samples were on average 6% lower than those of filtered and diluted equivalents (Vaselli et al. 2003) that were collected on the same dates in 1998–2001.

Similar effects from storage of untreated samples were also attributed to gypsum precipitation by Rowe et al. (1992b).

The samples collected between July 2004 and November 2006 were analyzed for sulfate, chloride and fluoride at OVSICORI-UNA in June–December 2006, using a fully automated microbore ion suppressed chromatographic system (Dionex ICS-3000) (Martínez 2008). The pH measurements were performed on untreated samples at ambient temperature (24 ± 2 °C) using a WTW Multi 340i potentiometer. Combination of the new results with previously available data (e.g. Casertano et al. 1985; Rowe et al. 1992a, b; Nicholson et al. 1992, 1993; Martínez et al. 2000) constitutes a record for major anion concentrations, pH and temperature that covers the period 1980–2006.

Dissolved unreacted SO_2 and H_2S gases in the lake water were measured in situ on an irregular basis during 1999–2006, using a gas detection tube method (Takano et al. 2008). Detection limits for dissolved SO_2 and H_2S were 1 and 0.2 ppm, respectively.

All field-related data (lake volume, temperature, color, seismic records, etc.) are from the database of OVSICORI-UNA (Venzke et al. 2002; Martínez et al. 2000; Martínez 2008). Most of the monthly rainfall data come from the Poás volcano summit rain gauge of the Centro de Servicios y Estudios Básicos de Ingeniería of ICE located at 2,564 m a.s.l.

Polythionates—Relationships with Lake Properties, Fumarolic Activity and Eruptive Phreatic Events

In the following sub-sections, variations in PT distributions and quantities are described in relation to the composition and behavior of the lake, on-shore fumarolic activity, supply of volatiles, eruptive phreatic (phreatomagmatic?) events, monitored seismicity, and microgravity survey for the lake activity stages distinguished by Martínez (2008).

Microgravity and PTs

Microgravity surveys detected an intriguing increase between 1996 and 2001 at stations near the N and NE lakeshores, possibly signaling a magmatic intrusion at depth, which must have been small and fairly localized since most of the other stations showed continuous decreases (Rymer et al. 2005, 2009). Gas release from this putative intrusion may first have induced the sudden re-appearance of large amounts of PTs in the lake in January 1996, followed by their sulfitolysis-induced disappearance due to substantial injection of fresh SO_2 into the lake between early 1998 and late 2002. The occurrence of a new fresh intrusion is also supported by the high C/S ratios and high equilibrium temperatures determined in the volatile phase by Fischer et al. (2015), enhanced CO2 and H2 diffuse emission rates (Melián et al. 2010; Melián et al. Chapter "Diffuse CO_2 Degassing and Thermal Energy Release from Poás Volcano, Costa Rica".), the appearance of low temperature sub-aerial fumaroles onshore the lake, the dome and the eastern sector of the crater, and the sustained increased in microgravity since 2001 until at least 2009 (Fig. 5) (Rymer et al. 2009; Rymer H pers. comm. 2010). Contemporary with these observations is the occurrence of a hydrothermal explosion in April 1996, and a composition of the lake water which was unusually enriched in chloride respect to sulfate between late 1997 and early 2004 (Fig. 6). The enrichment of the lake water in chloride suggests the degassing of a "fresh body of magma" underneath the region that comprises the lake and the dome that started intruding at shallower levels sometime between the mid 1990s (1996–1999) and the early 2000s that might have triggered the 2006–2014 phreatic cycle (Stage V) (Rymer et al. Chapter "Geophysical and Geochemical Precursors to Changes in Activity at Poás Volcano"). A new magmatic intrusion might have started between 2015 and 2016, according to some seismic patterns (recording of discrete short duration harmonic tremor which is

unusual at Poás) and chemical changes of the acid lake. We suggest that the phreatomagmatic eruptions of April 2017 is the surface manifestation of the 2015–2016 intrusion event.

Seismicity

Numerous swarms of A-type earthquakes and an intensification of AB-type seismicity between the end of 1996 and the first months of 1997 had preceded the initial increase in volatile concentrations, whereas remarkably sustained volcanic tremors between October 1997 and March 1998 preceded the disappearance of PTs in April 1998. In addition, a short-lived increase in A and B-type seismicity was observed (Fig. 5). Whereas at Poás tremors generally occur in short discontinuous events, a single episode on 21 February 1998 carried on for 2.5 h, and 55 h of tremor were recorded during the whole month. This incidence of sustained tremor possibly reflected a continuous rise of magmatic/hydrothermal fluids in conduits that on one hand reached the lake bottom, increasing the input of volatiles and heat, and on the other fuelled the new fumaroles onshore around the lake.

The enhancement of hydrothermal activity (sub-aerial fumaroles around the dome, at other locations around the lake and along the lower part of the eastern edge, appearance of thermal springs) within the crater area between 1999 and October 2001 coincided with increased levels of B- and AB-type seismicity after two and a half years of relative quiescence (Fig. 5), suggesting a stronger interaction between the subsurface heat source and the hydrous system beneath the crater. Tremor, which was rare in 1999, took place for less than 30 min per day in September–November 1999 when the plume from the dome reached maximum heights (Fig. 9). Several unusual low-frequency earthquakes with periods of 40–175 s were recorded in this period as well (V Barboza pers comm 2005). An exceptional increase in tremor (a total of 108 h were recorded in September 2001, of which 7% corresponded to monochromatic tremor) coincided with the peak in PT concentrations observed in September–October.

Upwelling

Although the lake had shown upwelling activity during most of sub-stages IVA and IVB, specifically in its central part and near the dome, with sulfur globules emerging from subaqueous vents, convection was more intense and sulfur globules appeared in larger abundances during September 1997–July 1998. In contrast, in September–November 1998 upwelling activity and evaporation were weak, although more vigorous sub-aerial fumaroles continued appearing on the eastern side of the dome. Throughout 2000 and 2001, the lake was entirely covered by an acidic whitish fog (HCl fumes?). In August–September 2001 large bubbles (ca. 3 m in diameter) were observed in the central part of the lake.

Fumarole Activity

From December 1997 and throughout 1998 when the PTs reached maximum concentrations, the gas plume was up to nearly 600 m above the dome. Between February 1999 and June 2000, an unusually strong plume rose from 0.7 to 2 km above the northern fractured side of the dome (the plume was ~ 2 km height in September 1999) (Fig. 9), and was seen from the capital city of San José at 35 km southeast of the crater.

By late 1998, the first appearance of weak low-temperature fumaroles (around 83–95 °C) was observed in the eastern sector of the crater. In July 1999, long concentric cracks and some ambient and boiling point springs (15–95 °C) appeared here as well, coinciding with a magnitude 3.2 earthquake (Richter scale) that was felt at the summit of the volcano on 18 July. More fumaroles and springs continued appearing in the same area in 2000 and 2001 (Duarte et al. 2003), most of which remained active till 2006–2007. The widening of cracks produced instability and collapses at the eastern terrace. The fumaroles in

the SW sector of the crater became more vigorous during the second half of 1999 when outgassing at the dome increased. In early 2000 these fumaroles weakened and eventually disappeared in June 2000 at the same time when degassing at the dome diminished and the gas-vapour plume returned to heights of 100–500 m (Venzke et al. 2002; Mora and Ramírez 2004). Gas condensates from the dome, collected in late 1999-early 2000, showed a significant increase in sulfate, chloride and fluoride concentrations, as the fumarole temperature did (188 °C in March 2000 on the north side of the dome) (Fig. 5) (Vaselli et al. 2003; Fernández et al. 2003).

Gas Fluxes

Infrequent gas remote-sensing measurements carried out during the IVB sub-stage suggest that the SO2 flux was of the same order of magnitude as the average of 90 tons per day recorded in February 1991 (Andres et al. 1992): In February 2001 the minimum average flux of SO_2 was about 40 tons per day (Fournier et al. 2001, 2002), and in March 2002 the flux averaged 61 tons per day (Galle 2002). Between the second half of 1999 and the first part of 2000 an increase in Rn emission through the crater floor was observed (García et al. 2003). Significant increases in soil temperature and diffuse H_2 and CO_2 emissions in the eastern sector of the crater recorded in 2000–2002 were considered as possible precursor of pending volcanic unrest (Melián et al. 2001, 2003, 2004, Chap. 6). Alternatively, the invasion of deep hot permeable zones by meteoric water becoming enriched in volatiles and undergoing redox reactions may explain the strong fumarolic activity around the dome, the opening of the new field in the eastern sector and the H_2 anomalies (Vaselli et al. 2003). Fracturing and subsequent increase in permeability of the volcanic edifice could have been triggered by ground deformation due to the presence of a dense, already crystallized magma body beneath the southern side of the lake

(Fournier et al. 2001) or by local tectonic earthquakes (Mora and Ramírez 2004).

Relationship Between PTs and Seismic Activity

Seismic activity at Poás is complex, due to the dynamics of the magmatic and hydrothermal systems, their interactions and the possible combination with tectonic processes (Fernández 1990; Rowe et al. 1992b; Martínez et al. 2000; Rymer et al. 2000). Predominant seismic signals are the B-type or low-frequency earthquakes and the AB-type or intermediate-frequency quakes (Fig. 5). The B-type earthquakes are presumably generated within a few hundred meters from the surface, are concentrated below the crater floor, and may reflect interaction of liquid-gas phases within fracture conduits or bubble formation/collapse in the hydrothermal system. The AB-type quakes were attributed mostly to fumarole-opening events. The A-type or high-frequency earthquakes (volcano-tectonic quakes) and the T-type or volcanic tremor are not as frequently observed as the B- and AB-type quakes, confirming the shallow character of most of Poás' seismic activity. The A-type quakes at Poás were related to tectonic readjustments within the local fault system that may or may not be triggered by regional subduction-related earthquakes (Fernández 1990). They were also associated with fracturing of the brittle carapace of a shallow magma body underlying the hydrothermal system (Casertano et al. 1987), or to mechanical fracturing of country rock, suggesting pressure build up in the system. The T-type seismicity was interpreted as a result of continuous movement of fluids or magma through a rigid medium (Aki et al. 1977; Fernández 1990).

Relationships between seismicity and PTs are difficult to evaluate for Stage II because of the scarcity of data. Despite high seismic activity and a high flux rate of SO_2 from dome fumaroles in the early 1980s, the lake was probably characterized by low PT concentrations with a

dominance of pentathionate (Fig. 5), indicative of H$_2$S-enriched gaseous input and relatively modest activity. This illustrates a particular feature at Poás, namely that the location of major fumarolic outgassing may distort a straightforward relationship between the overall status and nature of degassing of the volcano and the behavior of the lake.

The strong rise in PT concentrations and the shift from pentathionate to tetrathionate dominance in early 1986 were associated with an initial increase in A-, AB- and B-type earthquakes as well as short-duration harmonic tremors after a relatively quiet period. The sharp drop in PT concentrations to below detection limits in early 1987, approximately 3 months before renewal of phreatic activity (Rowe et al. 1992b), coincided with a more conspicuous increase in seismicity, in particular B-type earthquakes. High levels of B-type seismicity remained throughout Stage III when the locus of fumarolic activity was centered within the lake area, and PTs remained virtually below detection limits (Fig. 5). The enhanced heat and volatile output could have been the result of an ascending magma beneath the lake, some time between 1985 and 1986, and/or subsurface hydrofracturing (Fernández 1990; Rowe et al. 1992a, b; Rymer et al. 2005). Peaks in A-type seismicity and tremor in 1990 and 1991 were interpreted in terms of this hydrofracturing, which did promote degassing but without the intrusion of new magma at that time (Fernández 1990; Rymer et al. 2000).

Some of the swarms of A-type quakes in 1994 coincided with large peaks in tremor (Fig. 5), strong degassing and the occurrence of phreatic explosions that may have been associated with renewed magma ascent (Martínez et al. 2000) or fracturing of the brittle envelope of the cooling magma present. Subsequent large variations in PTs contents in the returning lake were accompanied by fluctuations in seismicity.

Changes in the contents and distribution of PTs during Stage IV, reflecting changes in the flow rate and/or in the SO$_2$/H$_2$S ratios of subaqueous fumaroles, coincided with periods of either high or low levels of seismicity. Most conspicuous is the fact that the transition from relatively low-to-much higher B- and AB-type activity around 1999 roughly coincided with the sulfitolytic decline of PTs. The enhanced input of SO$_2$-rich volatiles may thus have been driven by stronger interaction between the magmatic and lake-hydrothermal systems. Following the brief quiet interval of Sub-stage IVC, the sudden rise of PTs, apparently prompted by an increase in volatile input, was accompanied by an increase in AB- and B-type seismicity and by uncommon tremors (Fig. 5). Some of these were also recorded in 1980 when magma was intruding, but in this case, given the lack of A-type earthquakes, the tremors was interpreted as a signal of fluid movement through pre-existing fractures (V Barboza pers. comm. 2005).

The reappearance of PTs in April 2005, their subsequent sulfitolytic or thermal breakdown and the renewal of phreatic explosions all point to the injection of hot SO$_2$-rich gas promoted by the opening of conduits and the rise of fluids, as signaled by swarms of A-type events and by a dramatic increase in AB-type seismicity that preceded and accompanied the large numbers of volcanic tremors registered throughout Stage V (Fig. 5). The monochromatic character of some of these tremors is usually related to movement of magma or magmatic/hydrothermal fluids at depth.

In summary, changes in the concentrations and speciation of the PTs in response to fluctuations in the rate and composition of gas/volatile input are often accompanied by changes in the activity or type of seismic signals. Increases in seismicity often come together with enhanced input into the lake, leading either to the production of PTs or to their breakdown when the flow rate of volatile and heat release reaches maximum levels. In other cases, the disappearance of PTs can be caused by weakening or shutdown of subaqueous fumarolic gas release, which is then supported by a decrease of seismic activity and changes in the lake properties as clearly observed during sub-stage IVC.

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