# Using Crater Lake chemistry to predict volcanic activity at Poás Volcano, Costa Rica

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**Abstract.** Monitoring of crater lake chemistry during the recent decline and disappearance of the crater lake of Poás Volcano revealed that large variations in $SO_4/Cl$, $F/Cl$, and $Mg/Cl$ ratios were caused by the enhanced release of HCl vapor from the lake surface due to increasing lake temperature and solution acidity. Variation in the concentration of polythionic acids ($H_2S_xO_6$, $x = 4$–6) was the most reliable predictor of renewed phreatic eruptive activity at the volcano, exhibiting sharp decreases three months prior to the initiation of phreatic eruptions in June 1987. Polythionic acids may offer a direct indicator of changing subsurface magmatic activity whereas chloride-based element ratios may be influenced by surface volatilization of HCl and subsequent recycling of acidic fluids in crater lake volcanoes.

## Introduction

Volcanic crater lakes represent a unique hazard because of the danger posed by the storage of large volumes of water in proximity to near-surface magma bodies. Explosive eruptions in crater lake settings can result in deadly lahars as seen at Mt. Ruapehu, New Zealand (O'Shea 1954) and Mt. Kelut, Java (Newmann Van Padang 1960). Development of geochemical indicators of impending eruptive activity at volcanos containing crater lakes is complicated by the fact that crater lakes may serve as high-level recycling centers for condensed volcanic fluids. Mass balance calculations for Poás volcano (Brantley et al. 1987; Rowe et al. 1992) indicate that seepage of crater lake brine and subsequent recycling affects crater lake chemistry and may also affect adjacent fumarole compositions. Care must therefore be taken when interpreting temporal trends of classical chemical indicators of volcanic activity such as S/Cl ratios in crater lake settings.

In this paper, the following two geochemical parameters measured at Poás Volcano from November 1984 to October 1990 are discussed: (1) chloride-based concentration ratios such as S/Cl and Mg/Cl (Menyailov 1975, Giggenbach 1974, 1983); and (2) the sulfur oxyanion species, polythionates (Takano 1987; Takano and Watanuki 1990). Variations in these parameters are examined and correlated with recent volcanic activity which accompanied the decline and disappearance of the crater lake in April 1989. Results at Poás suggest that sharp changes in chloride-based element ratios may result from surface processes only indirectly related to renewed magmatic activity whereas changes in lake water polythionic acid concentrations appear to occur independently of changing lake temperature and composition. At Poás, sharp declines in crater lake polythionic acid concentration preceded the renewal of phreatic eruptions in the crater lake by three months suggesting that variations in crater lake polythionic acid concentrations can be used as a sensitive and accurate indicator of impending lake phreatic activity.
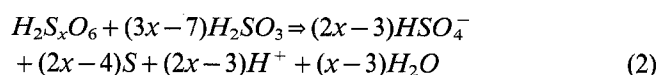
## Background

### Geochemical Parameters

Monitoring of S/Cl and F/Cl concentration ratios in crater lake waters is based on the common practice of monitoring these ratios in condensates from volcanic gas and fumaroles (e.g. Stoiber and Rose 1970). Changes in S/Cl and F/Cl ratios of gas and condensate samples prior to or during eruptive activity have been noted by several workers (Naughton et al. 1975; Hirabayashi et al. 1982; Williams et al. 1986). Increases in lake water $SO_4/Cl$ ratios prior to, or during eruptive activity, have been noted in the crater lakes of Zavaritsky volcano (Menyailov 1975) and Kusatsu-Shirane volcano, Japan (Takano and Watanuki 1990). The Mg/Cl ratio has been used along with pH variations at the crater lake of Mt. Rua-

pehu, New Zealand to monitor changes in fumarole injection rates and high-temperature water/rock interaction episodes (Giggenbach 1974, 1983; Giggenbach and Glover 1975). Increases in the Mg/Cl ratio at Ruapehu occur both during and after eruptive periods whereas long periods of relatively constant Mg/Cl ratios precede renewed volcanic activity. Thus, extended periods of constant Mg/Cl values in the lake may be used to predict periods of enhanced eruptive probability (Giggenbach 1983).

The monitoring of crater lake polythionic acid concentrations to predict phreatic or phreato-magmatic eruptions in crater lake volcanos was developed by Takano (1987) and Takano and Watanuki (1990) based on observations made at the crater lake in Yugama crater, Kusatsu-Shirane volcano, Japan. These workers reported a strong correlation between changing polythionic acid concentrations and recorded seismic and phreatic activity at Yugama. In particular, polythionic acid concentrations at Yugama declined below detection limits two months prior to renewed lake phreatic activity in October 1982. Polythionic acid concentrations increased during the short quiescent periods between explosions and then decreased with increasing volcanic activity (explosions and volcanic earthquake swarms). Declining polythionate concentrations have been attributed to sulfitolysis, a complex series of chain-shortening reactions which break down polythionic acids (Takano and Watanuki 1990). Sulfitolysis of polythionic acids occurs when gas of high $SO_2/H_2S$ ratio is injected into solutions containing polythionic acids. Under the extremely acidic conditions of a lake such as Poás (pH $\approx$ 0), the overall reaction sequence is perhaps best represented as:

$$SO_2 + H_2O \Rightarrow H_2SO_3 \qquad (1)$$

$$H_2S_xO_6 + (3x - 7)H_2SO_3 \Rightarrow (2x - 3)HSO_4^- + (2x - 4)S + (2x - 3)H^+ + (x - 3)H_2O \qquad (2)$$

(Takano and Watanuki 1990). At higher temperatures, thermal dissociation of polythionates will also occur:

$$3H_2S_xO_6 + 2H_2O \Rightarrow 5HSO_4^- + 5H^+ + (3x - 5)S^0 \qquad (3)$$
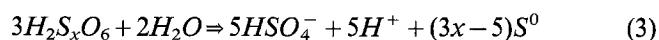
The final decomposition products of these reactions are elemental sulfur and sulfate thereby accounting for the inverse correlation between polythionic acid and sulfate concentrations observed at Yugama crater lake (Takano and Watanuki 1990). However, injection of $H_2S$-rich gases into an $SO_2$-saturated solution can increase the concentration of polythionic acids; increasing polythionic acid concentrations were correlated with periods of enhanced volcanic seismicity associated with the release of $H_2S$-rich fumarolic gases (Takano and Watanuki 1990).

## Poás Volcano

Poás Volcano, along with the adjacent volcanic centers of Platanar-Porvenir, Barva, Irazú and Turrialba forms the Cordillera Central, one of two Quaternary volcanic
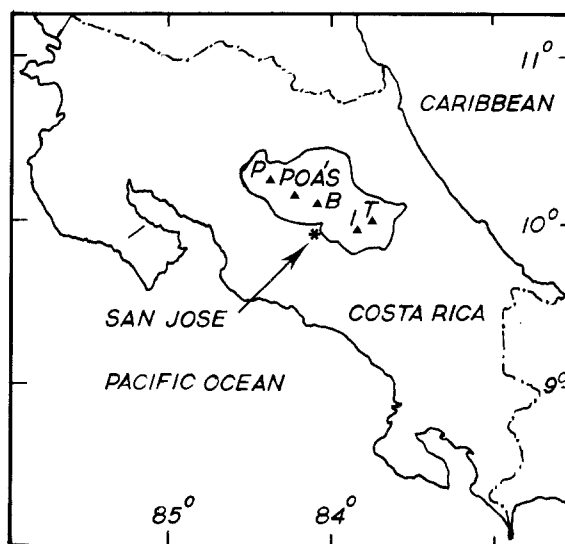


Fig. 1. Location map of Poás Volcano. Central outlined area covers volcanic deposits of the Cordillera Central, consisting of five overlapping volcanic centers including Platanar-Porvenir (P), Poás, Barva (B), Irazú (I), and Turriabla (T)

ranges in Costa Rica (Fig. 1). The active crater, the site of all historic activity at Poás, hosts a hot, acidic crater lake known locally as Laguna Caliente. When full, the lake possesses a diameter of about 300 m and a depth of approximately 55 m (Rowe et al. 1992). Like Yugama, Laguna Caliente waters are classified as acid chloride-sulfate brines (Brantley et al. 1987). However, in general, Poás lake waters are hotter than Yugama waters and are much more concentrated, exhibiting anion and cation contents one to two orders of magnitude greater than those of Yugama.

Volcanic activity at Poás has been varied and nearly continuous since the active crater was first visited in 1828 and includes nearly constant fumarolic activity, frequent geyser-like phreatic eruptions in the crater lake and rare phreato-magmatic eruptions (Casertano et al. 1983). The last-phreato-magmatic eruption at Poás in 1953-1954, was preceded by increasingly intense lake phreatic activity and a decline in lake level. Emission of juvenile ash and bombs in May 1953 coincided with the complete dessication of the lake; later strombolian activity formed a pyroclastic cone (dome) cored by basaltic-andesitic lava. The crater lake reformed in 1965 in a small pit crater north of the dome; vigorous episodes of lake phreatic activity were observed in the years 1972-1974 and 1976-1979 (Casertano et al. 1983).

Lake phreatic activity subsided in 1980; however, temperatures of fumaroles located on the dome adjacent to the lake rose from <100°C in 1980 to greater than 960°C by March 1981 following a two-week period of intense seismic activity in July 1980 (Casertano et al. 1983, 1985). Dome fumarole temperatures have exhibited variable but generally decreasing temperatures since 1981 with temperatures recorded after 1989 nearly always less than 100°C (Rowe et al. 1992). Slow decline of lake level without subsequent recovery during the rainy season started in 1980 (about 1 to 2 m/yr). Lake level

**Table 1.** Poás Crater Lake compositional data

| Date | Temp (°C) | Dens (20°C) (g/cc) | pH (20°C) | [Na$^+$] (mg/kg) | [K$^+$] (mg/kg) | [Ca$^{2+}$] (mg/kg) | [Mg$^{2+}$] (mg/kg) | [Fe]T (mg/kg) | [Al$^{3+}$] (mg/kg) | [Br$^-$] (mg/kg) | [F$^-$] (mg/kg) | [Cl$^-$] (mg/kg) | [SO$_4$] (mg/kg) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Yugama 8/8/60 | 33 | NR | 1.00 | 66.5 | 29.7 | 466 | 78 | 216 | 382 | NR | NR | 2760 | 3510 |
| AVG1980–81 | 44 | NR | 0.09 | 1400 | 440 | 940 | 1330 | 2160 | 4790 | NR | NR | 18830 | 60100 |
| 11/28/84 | 48 | 1.059 | 0.07 | 710 | 270 | ND | 780 | 1180 | 1670 | 47 | 1500 | 23700 | 57700 |
| 1/24/85 | 44 | 1.055 | 0.14 | 770 | 300 | 1200 | 790 | 1400 | 3000 | ND | 1660 | 25400 | 49500 |
| 3/20/85 | 44 | 1.054 | 0.13 | 690 | 270 | 1100 | 710 | 1300 | 2700 | ND | 1560 | 24700 | 48200 |
| 5/6/85 | 44 | 1.055 | 0.14 | 610 | 220 | ND | 690 | 1030 | 1510 | 50 | 1400 | 22000 | 55000 |
| 8/22/85 | 45 | 1.053 | 0.17 | 510 | 240 | ND | 600 | 910 | 1350 | 43 | 1280 | 21100 | 54200 |
| 10/9/85 | 45 | 1.051 | 0.18 | 535 | 240 | ND | 580 | 980 | 1350 | 49 | 1260 | 20700 | 52900 |
| 2/4/86 | 38 | 1.046 | 0.26 | 450 | 160 | ND | 560 | 780 | 1210 | 37 | 1010 | 16500 | 36900 |
| 5/2/86 | 38 | 1.043 | 0.20 | 470 | 190 | ND | 530 | 800 | 1250 | 46 | 970 | 16500 | 40100 |
| 8/23/86 | 52 | 1.041 | 0.20 | 450 | 165 | ND | 550 | 780 | 1170 | 33 | 1020 | 18900 | 41200 |
| 10/31/86 | 54 | 1.051 | 0.14 | 430 | 220 | ND | 500 | 810 | 1200 | 34 | 1240 | 23200 | 52000 |
| 1/10/87 | 61 | 1.069 | −0.01 | 520 | 250 | 2335 | 550 | 1020 | 2070 | 60 | 1590 | 30400 | 64400 |
| 2/27/87 | 62 | 1.076 | −0.03 | 600 | 280 | ND | 620 | 1020 | 1600 | 69 | 1750 | 33700 | 78600 |
| 3/19/87 | 62 | 1.089 | 0.00 | 680 | 310 | ND | 680 | 1130 | 1780 | 77 | 1820 | 35900 | 82900 |
| 7/12/87 | 68 | 1.066 | 0.03 | 510 | 240 | ND | 560 | 890 | 1440 | 66 | 1550 | 28900 | 64400 |
| 7/27/87 | 66 | 1.114 | −0.27 | 890 | 440 | ND | 830 | 1460 | 2370 | 91 | 2110 | 44900 | 103000 |
| 9/10/87 | 65 | 1.116 | −0.23 | 870 | 430 | ND | 840 | 1510 | 2400 | 100 | 2060 | 43400 | 108000 |
| 11/27/87 | 61 | 1.111 | −0.24 | 610 | 280 | 1060 | 500 | 1290 | 2500 | 110 | 1910 | 48000 | 101000 |
| 1/16/88 | 64 | 1.139 | −0.37 | 840 | 480 | 950 | 840 | 2040 | 3940 | 130 | 2250 | 59300 | 127000 |
| 3/2/88 | 60 | 1.118 | −0.31 | 750 | 460 | ND | 740 | 1500 | 2520 | 120 | 2100 | 51300 | 118000 |
| 6/24/88 | 65 | 1.181 | −0.61 | 1150 | 760 | 1340 | 1040 | 3040 | 5670 | 200 | 2970 | 73100 | 175000 |
| 9/2/88 | 75 | 1.208 | −0.53 | 1560 | 1100 | ND | 1520 | 3450 | 5100 | 234 | 3810 | 44200 | 196000 |
| 10/26/88 | 65 | 1.191 | −0.43 | 1510 | 1070 | ND | 1420 | 3750 | 4981 | 260 | 4220 | 47400 | 192000 |
| 2/7/89 | 87 | 1.305 | −0.87 | 2870 | 2400 | 90 | 3590 | 7060 | 18300 | 590 | 10400 | 28000 | 286000 |
| 3/3/89 | 82 | 1.247 | −0.55 | 3680 | 2280 | ND | 3650 | 7690 | 7400 | 410 | 6310 | 27200 | 233000 |
| 5/31/89 | 80 | 1.156 | −0.09 | 2660 | 1480 | ND | 2470 | 4710 | 8940 | 250 | 6150 | 25100 | 124000 |
| 6/9/89 | 77 | 1.209 | −0.40 | 3270 | 2080 | ND | 2780 | 5980 | 11000 | 330 | 8650 | 27700 | 188000 |
| 6/16/89 | 80 | 1.205 | −0.42 | 3060 | 1940 | ND | 2670 | 5510 | 10300 | 330 | 8090 | 34900 | 174000 |
| 6/22/89 | 80 | 1.220 | −0.44 | 3100 | 2240 | ND | 2840 | 6100 | 10600 | 420 | 8420 | 40600 | 175000 |
| 7/26/89 | 85 | 1.234 | −0.55 | 3370 | 2250 | ND | 2740 | 5910 | 10700 | 350 | 8600 | 46500 | 175000 |
| 8/3/89 | 85 | 1.222 | −0.46 | 3840 | 2260 | ND | 3420 | 6300 | 11200 | 280 | 7560 | 45400 | 163000 |
| 8/8/89 | 87 | 1.199 | −0.44 | 2720 | 1730 | 650 | 2040 | 5770 | 13700 | 400 | 8960 | 46300 | 167000 |
| 8/17/89 | 87 | 1.174 | −0.36 | 2590 | 1520 | ND | 2500 | 4700 | 8710 | 340 | 7230 | 39200 | 99300 |
| 10/24/89 | 82 | 1.213 | −0.56 | 2960 | 1810 | ND | 2630 | 5160 | 9630 | 420 | 7910 | 64100 | 154000 |
| 1/26/90 | 85 | 1.144 | −0.29 | 1830 | 1240 | ND | 1630 | 3790 | 6370 | 250 | 6400 | 52000 | 109000 |
| 2/21/90 | 90 | 1.169 | −0.56 | 2170 | 1360 | ND | 2070 | 4070 | 7830 | 450 | 8460 | 95200 | 103000 |
| 3/17/90 | 79 | 1.241 | −0.60 | 3080 | 2030 | 170 | 2650 | 5640 | 8760 | 480 | 8730 | 63100 | 165000 |
| 7/10/90 | ~80 | 1.130 | −0.44 | 1770 | 1300 | 330 | 1600 | 9560 | 10300 | 190 | 15400 | 90000 | 96700 |
| 9/13/90 | ~80 | 1.130 | −0.70 | 2320 | 2620 | 4800 | 2290 | 11500 | 13000 | 1820 | 25400 | 129000 | 102000 |

**Table 1.** (continued)

| Date | [H$_2$S$_4$O$_6$] (mg/kg) | [H$_2$S$_5$O$_6$] (mg/kg) | [H$_2$S$_6$O$_6$] (mg/kg) | [H$_2$S×O$_6$]T (mg/kg) | TDS (g/kg) | SO$_4$/Cl | F/Cl | Mg/Cl | [H$_2$S×O$_6$]T /[F] |
|---|---|---|---|---|---|---|---|---|---|
| Yugama 8/8/60 | 370 | 480 | NR | 850 | 8.5 | 1.27 | NR | 0.028 | NR |
| AVG1980–81 | NR | NR | NR | NR | 91.1 | 3.20 | NR | 0.071 | NR |
| 11/28/84 | 84 | 413 | 98 | 595 | 89.1 | 2.43 | 0.063 | 0.033 | 0.40 |
| 1/24/85 | 1202 | 2135 | 775 | 4112 | 88.0 | 1.95 | 0.065 | 0.031 | 2.48 |
| 3/20/85 | 1126 | 1773 | 517 | 3416 | 84.6 | 1.95 | 0.063 | 0.029 | 2.19 |
| 5/6/85 | 457 | 1190 | 363 | 2010 | 85.4 | 2.50 | 0.064 | 0.031 | 1.44 |
| 8/22/85 | 977 | 1750 | 528 | 3254 | 84.3 | 2.57 | 0.061 | 0.028 | 2.54 |
| 10/9/85 | 606 | 1281 | 461 | 2348 | 81.9 | 2.56 | 0.061 | 0.028 | 1.86 |
| 2/4/86 | 1170 | 1433 | 520 | 3123 | 61.6 | 2.24 | 0.061 | 0.034 | 3.09 |
| 5/2/86 | 1745 | 1828 | 634 | 4207 | 65.9 | 2.43 | 0.059 | 0.032 | 4.34 |
| 8/23/86 | 1710 | 1677 | 522 | 3909 | 69.1 | 2.18 | 0.054 | 0.029 | 3.83 |
| 10/31/86 | 1047 | 1323 | 423 | 2793 | 83.4 | 2.24 | 0.053 | 0.022 | 2.25 |
| 1/10/87 | 1573 | 1378 | 624 | 3575 | 106.7 | 2.12 | 0.052 | 0.018 | 2.25 |
| 2/27/87 | 169 | 639 | 117 | 925 | 119.9 | 2.33 | 0.052 | 0.018 | 0.53 |
| 3/19/87 | 53 | 71 | 0 | 124 | 126.2 | 2.31 | 0.051 | 0.019 | 0.07 |
| 7/12/87 | 709 | 1159 | 391 | 2159 | 101.6 | 2.23 | 0.054 | 0.019 | 1.39 |
| 7/27/87 | 2 | 6 | 0 | 8 | 156.7 | 2.29 | 0.047 | 0.018 | 0.00 |
| 9/10/87 | 0 | 0 | 0 | 0 | 160.2 | 2.49 | 0.047 | 0.019 | 0.00 |
| 11/27/87 | 0 | 0 | 0 | 0 | 157.8 | 2.10 | 0.040 | 0.010 | 0.00 |
| 1/16/88 | 0 | 0 | 0 | 0 | 198.0 | 2.14 | 0.038 | 0.014 | 0.00 |
| 3/2/88 | 0 | 0 | 0 | 0 | 178.1 | 2.30 | 0.041 | 0.014 | 0.00 |
| 6/24/88 | 0 | 0 | 0 | 0 | 269.1 | 2.39 | 0.041 | 0.014 | 0.00 |
| 9/2/88 | 0 | 0 | 0 | 0 | 257.5 | 4.43 | 0.086 | 0.034 | 0.00 |
| 10/26/88 | 0 | 0 | 0 | 0 | 257.1 | 4.05 | 0.089 | 0.030 | 0.00 |
| 2/7/89 | 0 | 0 | 0 | 0 | 359.6 | 10.21 | 0.371 | 0.128 | 0.00 |
| 3/3/89 | 0 | 0 | 0 | 0 | 292.7 | 8.57 | 0.232 | 0.134 | 0.00 |
| 5/31/89 | 110 | 6 | 0 | 115 | 176.6 | 4.94 | 0.245 | 0.098 | 0.02 |
| 6/9/89 | 207 | 44 | 0 | 251 | 250.5 | 6.79 | 0.312 | 0.100 | 0.03 |
| 6/16/89 | 55 | 2 | 0 | 57 | 241.5 | 4.99 | 0.232` | 0.077 | 0.01 |
| 6/22/89 | 0 | 0 | 0 | 0 | 249.8 | 4.31 | 0.207 | 0.070 | 0.00 |
| 7/26/89 | 255 | 89 | 25 | 369 | 256.2 | 3.76 | 0.185 | 0.059 | 0.04 |
| 8/3/89 | 696 | 613 | 213 | 1521 | 244.9 | 3.59 | 0.167 | 0.075 | 0.20 |
| 8/8/89 | 415 | 553 | 135 | 1103 | 250.4 | 3.61 | 0.194 | 0.044 | 0.12 |
| 8/17/89 | 0 | 0 | 0 | 0 | 166.8 | 2.53 | 0.184 | 0.064 | 0.00 |
| 10/24/89 | 0 | 0 | 0 | 0 | 249.3 | 2.40 | 0.123 | 0.041 | 0.00 |
| 1/26/90 | 22 | 18 | 0 | 40 | 183.3 | 2.10 | 0.123 | 0.031 | 0.01 |
| 2/21/90 | 16 | 11 | 0 | 27 | 225.8 | 1.08 | 0.089 | 0.022 | 0.00 |
| 3/17/90 | 0 | 0 | 0 | 0 | 260.0 | 2.61 | 0.138 | 0.042 | 0.00 |
| 7/10/90 | ND | ND | ND | ND | 229.8 | 1.07 | 0.171 | 0.018 | ND |
| 9/13/90 | ND | ND | ND | ND | 295.8 | 0.79 | 0.197 | 0.018 | ND |

Reported concentrations are density corrected. AVG1980–81 = average concentrations for eight samples collected between November 1980 and June 1981 by Casertano et al. (1985). Data for samples collected in January 1985 and January 1987 from Brantley et al. (1987). For comparison, an analysis of Yugama crater lake water from Kusatsu-Shirane Volcano, Japan (Takano and Watanuki 1990) is given at the top of the table

*ND*, no data; *NR*, not reported

decline accelerated after 1984, declining approximately 40 m from late 1984 to early 1989 with water losses exceeding 10$^6$ m$^3$ (Rowe et al. 1992). Geyser-like phreatic eruptions resumed in June 1987 following a seven-year quiescent period and continued with varying frequency and intensity through November 1988 (Smithsonian Institution 1987, 1988a, 1988b). Disappearance of the crater lake in April 1989 was immediately followed by several weeks of phreatic activity which ejected lake sediments, native sulfur and other non-juvenile lithic material to heights of 1-2 km (Smithsonian Institution 1989a, 1989b, 1989c). The lake reformed briefly during the rainy season of 1989 but dried up again in April 1990. Eruptive activity following the second disappearance of the lake was less intense than that observed in the previous year (Smithsonian Institution 1990a). Vig-

orous fumarolic venting of steam and gases along with sulfur cones and pits filled with liquid sulfur plus sediment mixtures were observed on the margins of the hot (80° C), acid lake through late 1990 (Smithsonian Institution 1990b).

The recent disappearance of the lake has been attributed to increased evaporation caused by an estimated doubling of the summit power output over the period 1/85–12/88 (Brown et al. 1989). The increase in heat flow was attributed to the upward ascent of fresh magma, inferred from crater-centered microgravity increases recorded over the period 1985–1989 (Rymer and Brown 1989; Brown et al. 1991). However, analysis of heat and water budgets of the crater lake over the period 1978–1989 by Rowe et al. (1992) suggests that the disappearance of the lake was due to the combined effects of sev-

eral years of below average rainfall over the period 1983–1989 and an increase in heat flow to the lake in 1987–1988. Based on analysis of available seismic and geochemical data Rowe et al. (1992) proposed that the increase in heat flow observed in 1987–1988 was caused by hydrofracturing of the upper portions of the cooling magma in late 1985-early 1986 with little or no ascent of new magma. These phenomena are considered further when interpreting the temporal variations in lake water chemistry described below.

## Sampling and analytical methods

Lake water samples analyzed for this study consisted of two groups. The first set consisted of six sample sets collected at approximately six-month intervals over the period 1987–1990. Samples of this group were filtered with 0.45 µm polycarbonate filters and diluted in the field to prevent precipitation of silica and gypsum. The second sample set is comprised of 50 lake water samples collected by personnel of the Observatorio Vulcanológico y Sismológico de Costa Rica of the Universidad Nacional at approximately monthly intervals since late 1984 for analysis of F, Cl and $SO_4$ concentrations, and pH. These samples were not diluted or filtered in the field. In March 1990 these samples were filtered and reanalyzed for species unaffected by secondary precipitation. Acid rain samples were collected from the west rim of the active crater. The rain gauge was directly downwind of the plume of acidic vapors issuing from the lake surface. The collector was open to the atmosphere so therefore represents the sum of both wet and dry acid deposition. All rain samples were filtered in the field using 0.45 µm polycarbonate filters.

Cations were analyzed using DCP-AES techniques on samples diluted by a factor of 10 to 100 using matrix-matched standards. The estimated analytical error is ±5% based on repeat determinations of control samples and standards. Sulfate, chloride, fluoride and bromide concentrations were determined with standard HPLC techniques on a Dionex 2010i ion chromatograph with estimated analytical errors of ±3%, ±3%, ±7% and ±15% respectively. Analytical errors for these species were obtained by running several repeat determinations on standards containing varying ratios of the anions of interest. Total error on measured sulfate concentrations of samples not diluted or filtered in the field is somewhat higher than the quoted analytical error due to the precipitation of gypsum during sample storage. High sulfate concentrations ($[SO_4]_{min} > 40000$ ppm) and relatively low calcium concentrations ($[Ca]_{max} < 2500$ ppm-measured on filtered and diluted samples) indicate a maximum total error of ±7% for sulfate in the non-diluted sample set. Individual and total polythionate concentrations on all samples were determined using sample preparation and ion chromatography techniques developed by Takano and Watanuki (1988). These workers demonstrated that polythionates concentrations greater than 100 ppm are stable for at least three years (and probably longer – cf. Takano and Watanuki 1990)

in highly acidic solutions (pH 0-2) chemically similar to those collected at Poás.

## Results

Since late 1984 lake temperature has varied from 38 to 96° C, densities of filtered samples at 20° C increased from 1.06 to 1.30 g/cm$^3$, and total dissolved solid contents have varied from 60 to greater than 350 g/kg (Table 1). Most rock-forming elements (e.g. Na, K, Mg, Fe and Al) exhibit a slight dilutional trend through 1986. Concentrations of these species then gradually increase, accelerating sharply in the months prior to the disappearance of the lake. Silica and calcium behave erratically or decline, suggesting that they are controlled by precipitation of amorphous silica and gypsum (Brantley et al. 1987). Sulfate and chloride concentrations increase as lake volume decreases up to mid-1988. However, chloride then decreased by a factor of three in the nine-month period preceding the disappearance of the lake whereas sulfate continues to increase. Concentration trends of fluoride parallel those of sulfate. Relatively little variation in the $SO_4/Cl$ ratio of Poás lake water is noted until mid-1988 despite the renewal of lake phreatic activity in June 1987. After mid-1988 the ratio exhibits a sharp increase peaking immediately prior to the disappearance of the lake in 1989; it then declines in a relatively steady fashion prior to mid-1990 (Fig. 2a). Temporal trends in F/Cl and Mg/Cl ratios are almost identical to that exhibited by the $SO_4/Cl$ ratio although the F/Cl ratio does increase through mid-1990 (Fig. 2b, c).

Total polythionic acid concentrations at Poás, normalized to fluoride concentrations to remove any dilutional effects, display sharp variations after late 1984 (Fig. 3a). Following a period of variable behavior, total polythionic acid concentrations rise sharply in late 1985 peaking at ≈4200 ppm in mid-1986. They decrease sharply in late 1986-early 1987 prior to the resumption of phreatic activity in June 1987. A sample taken on 12 July 1987 contains over 2000 ppm of polythionic acids while all later samples are at or below detection limits (<1 ppm) until mid-March of 1989. Samples taken over a three month period in mid-1989 display sharp variations in polythionic acid concentration (0–1500 mg/kg) before declining below detection limits for most of the latter half of 1989 and early 1990. Rising polythionic acid concentrations in late 1985-early 1986 are correlated with an increase in the number of low frequency microtremors (Type B seismicity) at Poás. Peak polythionic acid concentrations are associated with a period marked by a swarm of high frequency, Type A seismic events in early 1986 which accompanied the rise in Type B seismicity (Fig. 3b). However, this correlation is absent in 1989 and 1990 when Type B seismicity is extremely high. No particular correlation with lake temperature is noted prior to mid-1986; however, polythionic acid concentrations begin to decline sharply in mid-1986 when lake temperature approaches 50° C (Fig. 3c).
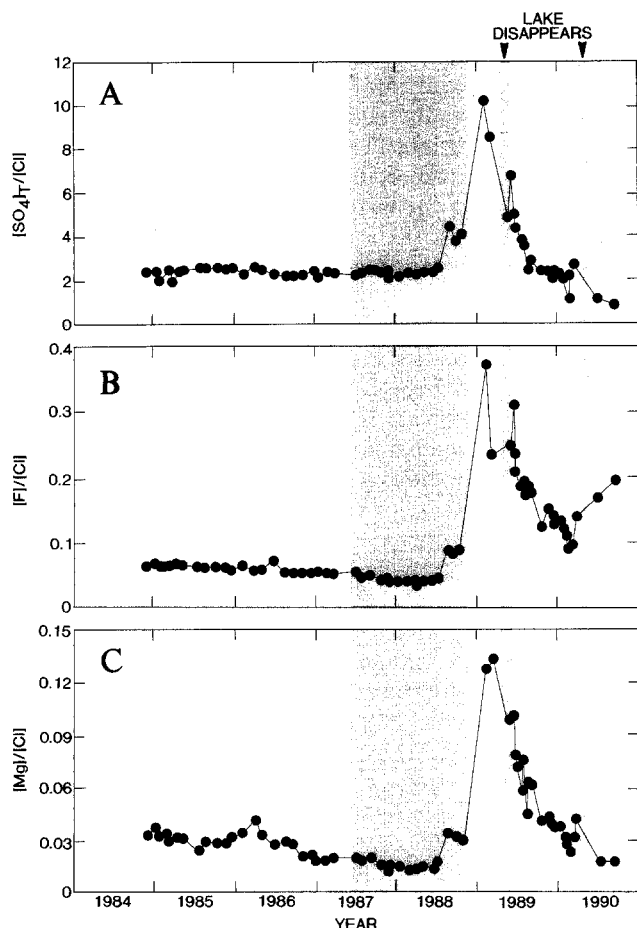
**Fig. 2 A–C.** Temporal variation in lake water SO$_4$/Cl (**A**), F/Cl (**B**), and Mg/Cl ratio (**C**). *Shoded* areas indicate periods of explosive phreatic activity. *Inverted pointers* indicate disappearance of lake in April 1989 and April 1990



**Fig. 3 A–C.** Temporal variation in lake water [H$_2$S$_x$O$_6$]/[F]$_T$ (**A**), Type B microtremor frequency (**B**), and lake water temperature (**C**). Also indicated is Type A seismic swarm of early 1986. All seismic and lake temperature data from Rowe et al. (1992)

Acid rain samples collected on the west rim of the active crater were analyzed for pH, F, Cl and SO$_4$ contents (Table 2). Large increases in acid rain chloride concentrations and a drop in pH are noted in the months preceding the lake disappearances in 1989 and 1990 (Table 2, Fig. 4a). The increased chloride content of the rain water samples is correlated with declining crater lake chloride concentrations and results in sharp declines in acid rain SO$_4$/Cl and F/Cl ratios.

## Discussion

### Chloride-based element ratios

The sharp increases in chloride-based element ratios observed in the months preceding the lake's disappearance in April 1989 are not due to increased fluxes of sulfate, fluoride or magnesium, but rather to a drop in lake chloride concentration (Table 1). We suggest that lake chloride concentrations declined due to the increased volatility of HCl as lake temperature and acidity increased. Vapor pressure data (Zeisberg et al. 1928; Fritz and Fuget 1956) for HCl solutions were used to estimate the

**Table 2.** Acid rain compositional data

| Date | pH (20° C) | [F$^-$] (mg/kg) | [Cl$^-$] (mg/kg) | [SO$_4$] (mg/kg) | SO$_4$/Cl | F/Cl |
|---|---|---|---|---|---|---|
| 3/85–6/86 | 2.90 | 3.6 | 22 | 36 | 1.636 | 0.164 |
| 1/19/88 | 3.04 | 0.4 | 26 | 12 | 0.458 | 0.014 |
| 6/26/88 | 1.00 | 10.0 | 3250 | 590 | 0.182 | 0.003 |
| 2/7/89 | 0.20 | 112 | 20600 | 228 | 0.011 | 0.005 |
| 8/8/89 | 2.60 | 2.7 | 107 | 53 | 0.496 | 0.025 |
| 3/17/90 | 1.30 | 19.4 | 4140 | 166 | 0.040 | 0.005 |

All samples collected on west rim of active crater with the exception of the 1985–1986 value. Value given for this period is the average value of 17 acid rain samples collected at the Cerro Pelon site ($\approx 0.5$ km south of west crater rim site) between May 1985 and June 1986 (Rosario-Alfaro et al. 1986)

chloride content of vapor in equilibrium with the lake surface as a function of temperature and total solution acidity. We note a strong correlation between calculated vapor concentrations and west rim acid rain chloride concentrations after mid-1988 (Fig. 4a). Lake water chloride contents decrease during the period of peak calculated HCl release (mid-1988 to April 1989) while acid
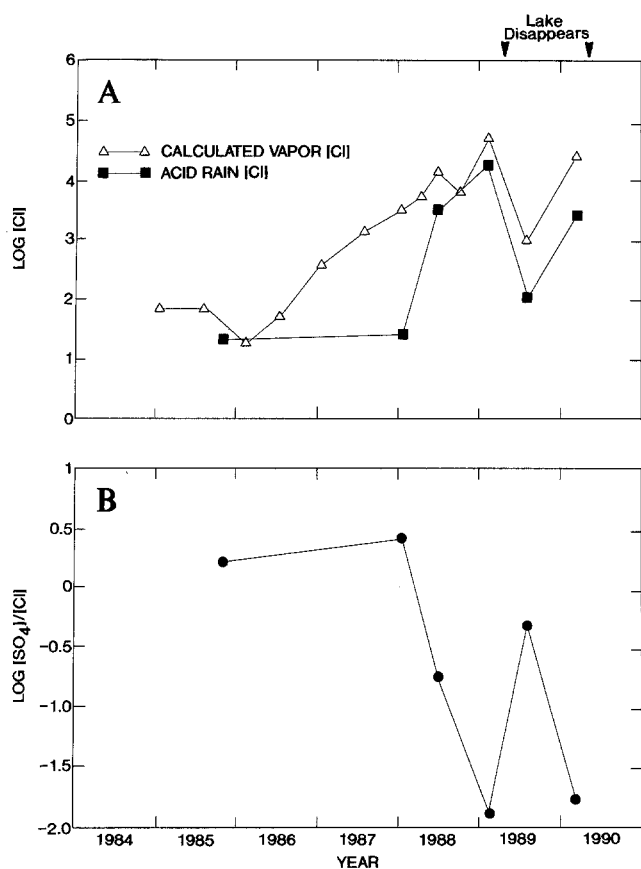
**Fig. 4A, B.** Lake vapor chloride concentrations versus acid rain chloride concentrations (**A**) and $SO_4/Cl$ ratios (**B**). Data from Table 2

rain $SO_4/Cl$ ratios decline sharply (Fig. 4b, Table 2). Acid rain samples taken in February 1989 display chloride concentrations in excess of 20000 ppm (approximately 0.55 N in HCl).

The extreme acidity of the lake brine at Poás allowed enhanced release of HCl vapor to occur despite relatively low temperatures. This is in marked contrast to the 360° C or higher temperatures required to distill HCl from near-neutral pH, chloride-rich fluids typical of the deeper portions of volcanic hydrothermal systems (Barnes 1984). February 1989 acid rain samples possess sulfate concentrations of only a few hundred ppm (Table 2). The partial pressure of gaseous $H_2SO_4$ over concentrated sulfuric acid solutions is extremely low; at the boiling point sulfuric acid solutions that are less than 85 wt% $H_2SO_4$ evaporate water exclusively so that loss of sulfate by surface volatilization is expected to be unimportant at Poás (Donovan and Salamone 1983). Surface volatilization of HCl gas thus selectively enriches crater lake fluid in sulfate over chloride producing an increase in the $SO_4/Cl$ ratio that could be interpreted as being indicative of renewed magmatic activity.

Significant volatilization of HF is not observed at Poás despite the fact that in dilute ($\leq 10$ wt%) pure acid solutions, HF is more volatile than HCl. Acid rain samples collected between January 1988 and March 1990 display F/Cl ratios that are typically an order of magni-

tude less than F/Cl ratios of crater lake water collected at the same time (Tables 1 and 2). This is attributed to extensive complexing of fluoride by aluminium whose concentration usually equals or slightly exceeds lake fluoride concentrations (Table 1). Modelling of chemical speciation in the lake brine suggests that $>95\%$ of the fluoride present in the water will be present as non-volatile Al-F complexes (Rowe 1991) thereby drastically reducing the concentration of $HF_{(aq)}$ available for volatilization.

Lake water Mg/Cl ratios exhibit a small peak in early 1986 (Fig. 2c). The first half of 1986 was marked by elevated Type A and Type B seismicity and sharp increases in fumarole condensate S and Cl concentrations (Rowe et al. 1992). These changes are attributed to hydrofracturing of the magmatic carapace (Rowe et al. 1992) and the subsequent release of magmatic volatiles beneath the lake. These phenomena would also be consistent with lake brine interaction with ascending fresh magma as proposed by Rymer and Brown (1989) and Brown et al. (1991). In either case, interaction of convecting lake brines with released magmatic fluids and/or fresh magmatic material could have caused the observed increase in the Mg/Cl ratio. However, magnesium concentrations after 1986 clearly parallel concentration trends exhibited by other conservative rock-forming elements (e.g. Na) so that significant water-magma interaction is ruled out after 1986.

The intense acidity and relatively high-temperature ($T > 70°$ C) of the lake brine in the months preceding the lake's disappearance are extreme when compared to other crater lakes (Zelenov 1969; Giggenbach 1974; Casadevall et al. 1984; Takano and Watanuki 1990). Such conditions do not exist in the majority of crater lake systems and did not exist at Poás prior to 1988; thus, chloride-based element ratios can still be useful in other crater lake volcanos. However, because seepage and recirculation of lake brine may be an integral feature of crater lake hydrothermal systems (Rowe et al. 1992), surface volatilization of HCl will result in a systematic shift in overall fluid chemistry towards higher S/Cl ratios. Recycling of such fluids could affect the interpretation of chemical trends in nearby fumaroles and thermal springs. Indeed, geochemical evidence presented by Rowe et al. (1992) suggests that fumaroles adjacent to the crater lake at Poás were contaminated by invading crater lake brines affecting fumarolic S/Cl and F/Cl ratios in mid-1984. Thus, care should be taken when evaluating temporal trends of fumarole or thermal spring chemistry in crater lake volcanos.

### Polythionic acid concentrations

The geochemical parameter which exhibited the most potential as an indicator of lake phreatic activity was the concentration of polythionic acids ($H_2S_xO_6$, $x = 4$-6). Polythionic acids are produced when $H_2S$ reacts with $SO_2$ in solution (Goehring 1952):

$$3SO_{2(aq)} + H_2S_{(aq)} \Rightarrow H_2S_4O_{6(aq)} \tag{4}$$
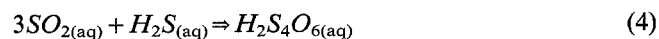
Experimental work by Ohsawa et al. (in preparation) indicates that polythionic acid speciation and stability in acidic solutions is a strong function of the $(SO_2/H_2S)_{(aq)}$ ratio of the reacting sulfur gases. Experiments carried out under acidic conditions (pH = 1.0) reveal that the optimum $(SO_2/H_2S)_{(aq)}$ ratio for the maximum formation of tetrathionic acid ($x = 4$) is three (i.e. Eq. 1); penta- and hexathionate ($x = 5, 6$) concentrations peak at $(SO_2/H_2S)_{(aq)}$ ratios near one. $(SO_2/H_2S)_{(aq)}$ ratio less than 0.2 result in small quantities of polythionates; $(SO_2/H_2S)_{(aq)}$ ratios greater than 10 also result in trace quantities of polythionic acids, but these gradually disappear due to sulfitolysis reactions which occur with high $SO_2/H_2S$ ratios.

Takano (1987) and Takano and Watanuki (1990) suggest that the breakdown of polythionic acids by sulfitolysis, in response to increases in the $SO_2/H_2S$ ratio of subaqueous fumaroles, explains why decreasing polythionic acid concentrations indicate impending eruptive activity. They assume that other variables such as degree of aeration, salinity, bulk compositional effects and lake temperature, do not affect polythionic acid stability. Indeed, oxidation of polythionates due to addition of atmospheric oxygen into lake water will be minimal because dissolved $O_2$ is readily reduced by $SO_2$. Potentially more important are bulk compositional effects on polythionic acid stability. Poás lake brines are typically an order of magnitude more concentrated than Yugama crater lake water and contain up to several thousand ppm iron and aluminum. Takano and Watanuki (1988) examined the catalytic effect of ferric iron on polythionate stability and found that the presence of high concentrations of ferric iron significantly reduced the stability of polythionates in Yugama crater lake waters. Ohsawa et al. (in preparation) report that during the period of declining polythionic acid concentrations in the latter half of 1986, the $Fe^{3+}/Fe^{2+}$ ratio of Poás lake water was less than 0.15 implying that ferric iron concentrations in the lake during this period were about an order of magnitude lower than observed polythionic acid concentrations (Table 1). Hence, the effect of ferric iron on polythionic acid concentrations was probably minimal.

The thermal stability of polythionic acids at elevated temperatures in highly acidic solutions is currently being investigated by Ohsawa et al. (in preparation). Heating of a Poás lake water collected on 8 August 1989 (Table 1) at 80° C resulted in complete breakdown of all polythionic acids in one week. Heating of the same sample to 130° C resulted in complete breakdown of all polythionates in a matter of hours. In contrast, heating of an artificially prepared polythionate solution (pH 1.0) at 80° C resulted in little decomposition of tetra- and pentathionate and the decomposition of only 28% of total hexathionate after three weeks. These results suggest that Poás lake water contains an unknown catalyst which is accelerating the breakdown of polythionic acids. Also, experiments conducted with Yugama water at 60° C revealed that polythionic acids initially declined to about half of their original concentration and then remained stable for up to three months. These preliminary results suggest that thermal decomposition of poly-

thionates is not the primary factor responsible for observed decreases in lake water polythionic acid concentrations, especially at lake temperatures less than 80° C. Instead, observed variations in polythionate concentrations in the lake may be due to variations in the $SO_2$ content of subaqueous fumaroles.

Consideration of chemical mass balance indicates that polythionic acids lost through lake bottom seepage must be replaced by the continual reaction of sulfur gases injected into the lake through lake bottom fumaroles. Production of polythionic acids by reaction of sulfur gases in the lake must occur because polythionic acids are unstable at the high temperatures ($> 150°$ C) experienced by the lake brines during circulation through the underlying liquid-dominated convection cell (see Rowe et al. 1992). Polythionic acid concentrations in excess of 1000 ppm in samples ranging in temperature from 38 to 87° C and ionic strength of 2 to 11 molal support the hypothesis that reactions responsible for forming polythionic acids occur under a wide temperature and compositional range. High ionic strength (9–11 molal) samples taken over a three-month period in mid-1989, which displayed sharp variations in polythionic acid concentration despite relatively constant lake chemistry and temperatures of 70–85° C, also suggest that changing polythionic acid concentrations reflect changes in an external variable, such as the $SO_2/H_2S$ ratio of lake bottom fumaroles.

Recorded $SO_2/H_2S$ ratios at Poás range from values greater than 100 for high temperature (T > 800° C) fumaroles collected in 1981–1983 to values less than 1 for low-temperature (T = 94–95°) lake bottom fumaroles sampled in February 1989 (Rowe et al. 1992). Changes in the $SO_2/H_2S$ ratio of Poás fumarolic gas samples reflect the temperature dependence of the following equilibrium:

$$SO_2 + 3H_2 \Leftrightarrow H_2S + 2H_2O \qquad (5)$$

The reaction is shifted to the left under conditions of high-temperature (T > 800° C), high oxygen fugacity or high water fugacity; the reaction shifts to the right under lower temperature, more reducing conditions. Restored equilibrium compositions of the high-temperature gases collected in 1981–1983 indicate that Poás gases are relatively oxidized, possessing $f_{O_2}$ values near the Ni-NiO oxygen buffer (Rowe 1991). Cooling calculations made with the computer code SOLVGAS (Symonds and Reed in press) assuming homogenous equilibrium in the gas phase, indicate that the oxygen fugacity of Poás gases is buffered near the Ni-NiO oxygen buffer. As a result, even at low temperatures, $SO_2/H_2S$ ratios of the Poás gases should never be less than 10. Thus, if low-temperature gases entering the lake bottom maintain homogeneous equilibrium during cooling, only trace quantities of polythionates can be expected to form in the crater lake.

However, high-temperature gases are likely to be severely modified by non-equilibrium processes during their ascent from the shallow magma to the lake bottom. Upon cooling, initially $SO_2$-rich gases will be increasingly buffered to a more reduced, $H_2S$-rich compo-

sition by fluid-rock reactions in lower temperature, brine-rich portions of the hydrothermal system. Ferrous iron present in wallrock is the reductant used to convert $SO_2$ to $H_2S$. The amount of $SO_2$ converted to $H_2S$ depends on the residence time of the gas in the liquid-dominated portion of the hydrothermal system (Giggenbach 1987). Thus, the intensity of degassing from the underlying magma body will play an integral role in determining the bulk $SO_2/H_2S$ ratio of gases entering the crater lake. Ascending $SO_2$-rich gases will also be subject to a variety of secondary reactions which result in a shift to $H_2S$-rich compositions. Especially important are the hydrolysis of elemental sulfur and $SO_2$, both of which produce $H_2S$ and $H_2SO_4$ at temperatures below approximately 250° C (Ellis and Giggenbach 1971; Giggenbach 1987).

We interpret the broad increase in polythionate concentration which occurs in early 1986 to represent enhanced gas release during heightened seismic activity (Fig. 4a, b). This seismic activity is hypothesized to represent a subsurface hydrofracturing event (Rowe et al. 1992) but could also represent ascension of fresh magma (Rymer and Brown 1989; Brown et al. 1991). Rising magmatic-temperature, $SO_2$-rich volatiles would be converted to $H_2S$ and $H_2SO_4$ as they encountered lower temperature, water-saturated zones beneath the lake resulting in a rise in polythionic acid concentrations in the lake water. Eventually, continued upward movement of heat and $SO_2$-rich volatiles would overwhelm the limited buffering capacity of the sub-lake hydrothermal system allowing gases of higher $SO_2/H_2S$ ratios to reach the lake bottom. Resulting sulfitolysis of existing polythionic acids would then cause the sharp decline in polythionic acids observed in late 1986-early 1987. This behavior is remarkably similar to the sharp declines in polythionic acid concentrations observed prior to renewed phreatic activity at Yumaga crater lake (Takano and Watanuki 1990). The absence of polythionic acids in crater lake brines from mid-1987 to late 1988 implies continued high release of $SO_2$-rich gases which is consistent with the elevated thermal power output observed over this time period (Rowe et al. 1992). Note, however, that initial indications of change in the subsurface hydrothermal system were provided by sharply rising polythionate concentrations which were coincident with enhanced microtremor activity in late 1985-early 1986 and which preceded the long-term increase in lake temperature (Fig. 4b, c). A correlation between rising polythionate concentrations and ensuing earthquake swarms was also noted at Yugama crater lake (Tanako and Watanuki 1990). This suggests that sharp increases in polythionate concentrations may provide notice of subsurface heating events several months before such changes are reflected at the surface.

## Conclusions

At Poás, concentrations of polythionic acids exceeding 1000 ppm occur over a wide range of temperature and composition. During periods of relatively constant lake

temperature and chemistry, sharp changes in the polythionic acid concentration were observed, suggesting that polythionic acid concentrations were responding to other variables. Elimination of temperature and chemical effects leaves changes in the $SO_2/H_2S$ ratio of subaqueous fumaroles as the most likely control on polythionate speciation and stability in the lake. At Poás, response was marked by almost complete disappearance of polythionates from the lake water three months before the first phreatic eruption, a pattern remarkably similar to that observed at Yugama crater lake, Kusatsu-Shirane volcano, Japan (Takano and Watanuki 1990). Perhaps more importantly, increasing concentrations of polythionic acids, which coincided with enhanced seismic activity in late 1985 and early 1986, provided a rapid response to the proposed magmatic activity of 1986, several months before more obvious indicators of impending eruptive activity, such as increasing lake temperature, were evident at the surface.

In contrast, more classical geochemical parameters used to monitor volcanic activity at crater lake volcanos such as Mg/Cl and $SO_4/Cl$ ratios gave little indication of the impending eruptive activity at Poás. Sharp rises in chloride-based elemental ratios in the months prior to the disappearance of the lake in April 1989 would be classically interpreted as evidence for the increased release of sulfur-rich magmatic gas. In contrast, we attribute the increase to the vaporization of HCl gas from the lake surface due to increasing lake temperature and solution acidity. Because seepage and subsequent recycling of crater lake brines is an important component of the heat and water budgets of the crater lake volcanos, volatilization of HCl will serve to shift overall system fluid chemistry to a more sulfur-rich composition. These effects may hamper the interpretation of temporal chemical trends in nearby fumaroles and thermal springs of volcanos possessing hydrothermal systems similar to Poás. However, monitoring crater lake chemistry as a function of volcanic activity allows testing of potentially valuable predictive tools and may well provide new insights for deciphering subtle subsurface magmatic events in active volcanos.

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