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Naturally acid waters from Copahue volcano, Argentina

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ABSTRACT

Volcanic acid sulfate–chloride brines form through absorption of volcanic vapors in shallow reservoirs of meteoric water. Reaction with surrounding volcanic rocks leads to partial neutralization of the fluids and precipitation of secondary minerals. Chemical data of such acid waters from Copahue volcano, Argentina, covering 8 years of observations, show evidence for changes in composition related to water rock interaction at depth prior to emergence of the fluids at the surface. The chemical composition changed dramatically during the 2000 eruption of Copahue, with enhanced concentrations and fluxes of Mg, Na, Fe and Al, followed in 2001 by rapidly declining concentrations and element fluxes. The subsequent 5 years saw more variable element ratios and strong depletions in K and Al. Most incompatible elements are released from the rock matrix stoichiometrically, whereas some elements are enriched through vapor input from the magma (As, Pb, Zn). Most fluids have LREE enrichments relative to the rock matrix, but during periods of new magma intrusion the LREE enrichment decreases as does the magnitude of the negative Eu anomaly in the fluids. These observations are interpreted assuming early dissolution of plagioclase, olivine and volcanic glass that occurs during intrusion of new magma into the hydrothermal system. The high field strength elements are virtually immobile even in these hot acid fluids, with Nb and Ta more so than Hf and Zr. The mobility of U and Th in these fluids is comparable, at variance with Th behavior in neutral fluids. The local rivers and lakes of Copahue are fertilized by volcanic dissolved P, and most surface waters with pH < 3 have high levels of As. The acid fluids from Copahue may be surficial analogs for deep subduction fluids that evolve below zones of arc magma generation as well as for early Mars environments that are thought to have had large acid lakes.

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1. Introduction

Acid fluids are common contaminants in the industrial world, ranging from acid rain to acid mine drainage to industrial waste fluids (Schuiling, 1998). Many volcanic regions carry acidic waters that are related to the oxidation of geothermal H₂S to H₂SO₄ in the shallow environment (Schoen and White, 1965; Schoen et al., 1974; Africano and Bernard, 2000). Such fluids have pH values of 2–3, are dominated by SO₄²⁻ but low in Cl. Another group of acid volcanic fluids are SO₄–Cl acid brines that are found in crater lakes, hot springs and the rivers that drain these source areas (e.g., Rowe et al., 1992a,b; Kempter and Rowe, 2000; Sriwana et al., 2000; Varekamp et al., 2000; Delmelle and Bernard, 2000a,b; Delmelle et al., 2000; Gammons et al., 2005). In general, these acid fluids form when magmatic gases such as SO₂, HCl and HF are captured by condensed volcanic waters with variable contributions of mete-

oric waters (e.g., Brimhall and Chiorso, 1983; Kusakabe et al., 2000; Varekamp et al., 2001; Symonds et al., 2001). The absorption of SO₂ in water leads to its disproportionation according to $3\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HSO}_4^- + 2\text{H}^+ + \text{S}$, generating acidity and solid S or liquid S when the temperature is high enough (Kusakabe et al., 2000; Symonds et al., 2001). These acid fluids then react with surrounding rocks and acquire rock forming elements (RFE) and trace elements. Some volatile trace elements may also be contributed by the primary magmatic gases. Such deep-seated volcano-hydrothermal fluids may be expunged into crater lakes or through hot springs, feeding naturally acidic rivers and lakes and lowering pH values down to zero (Rowe et al., 1995; Kempter and Rowe, 2000; Sriwana et al., 1998; Delmelle and Bernard, 2000a,b; Gammons et al., 2005).

The composition of volcano-hydrothermal acid fluids probably closely mimics that of hydrothermal fluids in direct contact with magmatic gases (Kusakabe et al., 2000). The changes in composition of such fluids over time has been used to monitor ongoing volcanic activity or forecast volcanic events (Giggenbach, 1974;

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Giggenbach and Glover, 1975; Rowe et al., 1992b; Takano et al., 1994; Christenson, 2000; Martinez et al., 2000; Varekamp et al., 2001). The chemistry of these acid fluids may also provide insights into the composition of ore-carrying fluids and the alteration patterns that they may cause (Barnes, 1979; Hedenquist et al., 1994).

The acid fluids from Copahue were studied in detail for their compositional variation during a volcanic eruption (Varekamp et al., 2001), as expressions of water–rock interaction (Varekamp et al., 2004), and for their changes in rare earth element (REE) contents during dilution and neutralization (Gammons et al., 2005). The evolution of Lake Caviahue and URA element fluxes were discussed by Pedrozo et al. (2001, 2008) and Varekamp (2003, 2008). Here compositional variations of the main Copahue hot springs and crater lake fluids over an 8-year period, which includes the period of volcanic eruptions of Copahue in 2000 (e.g., Delpino and Bermudez, 2002) are discussed, and the Copahue fluids compared with data from other acid volcanic fluids.

2. Geographic setting

Copahue volcano (37.5°S, 71°W, 2980 m above mean sea level) sits on the rim of the large ~2 Ma Caviahue caldera in the province of Neuquen, Argentina (Bermudez and Delpino, 1995; Delpino and Bermudez, 1995; Varekamp et al., 2006). Copahue volcano (Fig. 1) has an acid crater lake (CPL, pH ~ 0.2–1.1) and acid hot springs (CP, pH ~ 0.3–2.4) near the summit that feed an acid river, the Upper Rio Agrio (URA, pH ~ 0.5–2.5). This river discharges into a large glacial lake (Lake Caviahue, CVL) that is acidified (pH ~ 2.1–2.7) and the Lower Rio Agrio (LRA; pH ~ 2.1–6) carries lake fluids outside the Caviahue caldera (e.g., Ouimette, 2000; Fehn et al., 2002; Gammons et al., 2005; Parker et al., 2008). After its exit from the caldera, “normal” rivers mix with the acid river, which leads to copious precipitation of orange–red to bright yellow hydrous Fe-bearing mineral phases. The river then continues with a water fall (El Salto) and flows east down the flank of the old Caviahue volcano. The LRA then mixes with the Rio Norquin and is further di-

luted and neutralized to arrive with a pH ~ 6–8 near the town of Loncopue to the South (Fig. 1). Many river boulders are colored dull red from episodic acidic pulses that reach these lower sections of the LRA during periods of high discharge from Lake Caviahue. Mudpots, geothermal pools, and gas vents occur on the north side of Copahue volcano, some with acidic waters, surface expressions of a large underlying geothermal system (Mas et al., 2000).

3. Sampling methods

Water samples were collected in the field with van Dorn bottles or large open bottles. The samples were filtered the same day through 0.2 µm filters, and the more concentrated fluids were diluted either 26 times or 52 times. Almost all samples had field pH values < 3, and these samples were not acidified. The more dilute river samples with pH > 3 were acidified with HNO₃ to a pH ~ 1. The temperature was measured in the field, together with the pH, either with a digital probe or with pH paper. The pH values reported here were re-measured in the lab at the local room temperature (22 °C) after calibration with pH standard fluids at 1, 4 and 7. Fluids with measured pH values below 1 were estimated through charge balance – speciation calculations with the ‘web-phreeq’ program (<http://www.ndsu.nodak.edu/web/phreeq/>), because measured pH values below one after calibration with NBS pH standards based on the extended Debye–Huckel approximation can deviate strongly from the ‘true values’ (e.g., Nordstrom et al., 2000). The pH values measured in the field at the local water temperature usually differ from the laboratory pH measurements at 22 °C because the pH changes during cooling as a result of changes in the SO₄²⁻ → HSO₄⁻ equilibrium (see Gammons et al., 2005, for a discussion). Small differences in pH values in low pH fluids represent large differences in H⁺ contents, and even if the pH measurements or calculations are precise at the second decimal, errors in H⁺ activity can still be substantial. Errors in H⁺ concentration (e.g., for charge balance calculations) are even larger because of the uncertainties in activity coefficients in these concentrated fluids.

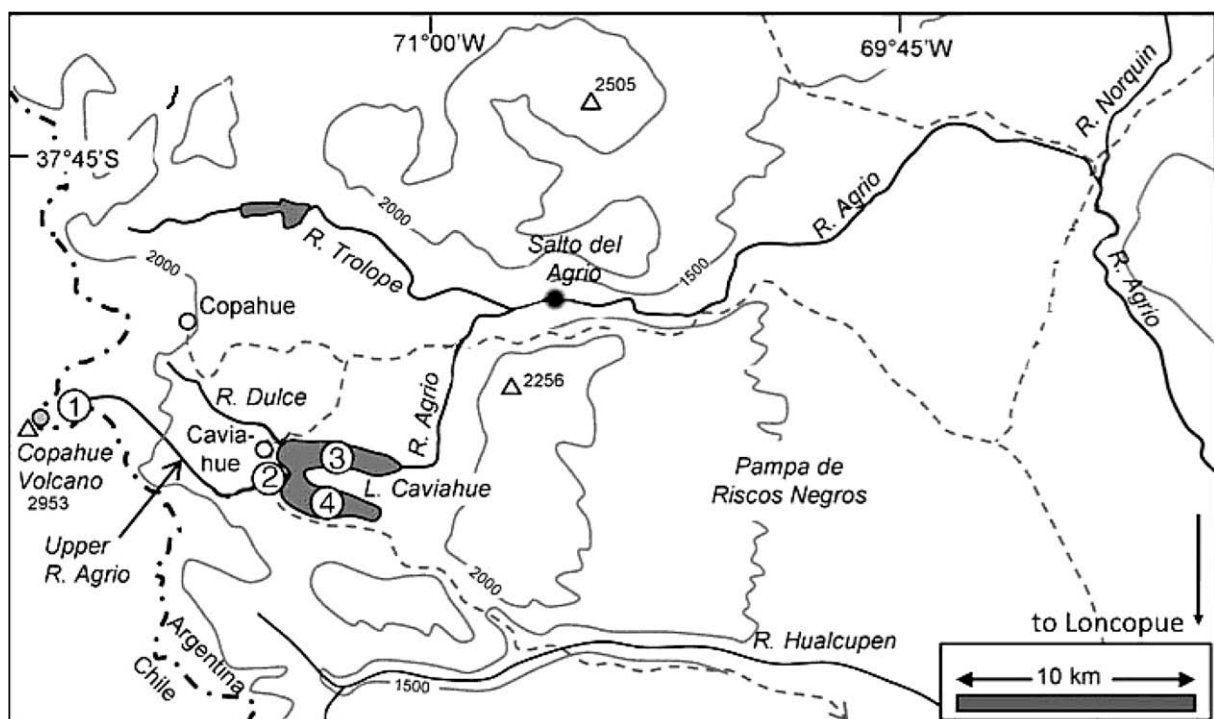


Fig. 1. Copahue volcano and its watershed: Copahue hot springs (CP, 1) and Copahue crater lake (CPL, 1), inlet of the Upper Rio Agrio (URA, 2) into the north and south arms of Lake Caviahue (CVL, 3, 4), Lower Rio Agrio (LRA), Salto (waterfall) of the LRA, and confluence of the LRA with the Rio Norquin (modified after Gammons et al., 2005).

The F–Cl–SO₄ concentrations were analyzed by ion chromatography (Dionex) at Wesleyan University and aliquots were analyzed at Amherst College (MA) on a similar Dionex instrument for QA/QC. Samples were also analyzed for bulk S by ICP-AES at Wesleyan University as well as at the CT Agricultural Experiment Station (New Haven, CT, USA). The most concentrated samples were also analyzed by gravimetry for total S (barite precipitation with the precipitate washed in oxalic acid for Fe-oxide removal prior to drying and weighing). The observed variations in SO₄ contents from these various techniques ranged between 1% and 5%, but averaged about ±1.5%.

Cations were analyzed by ICP-AES and ICP-MS at SGS Minerals Services (Ontario, Canada) and by ICP-AES at Wesleyan University. The major elements were taken from the ICP-AES analyses of diluted aliquots, whereas the trace element data were used where possible from the ICP-MS analyses. In a few samples (e.g., most URA samples) only ICP-AES data were available and these trace element analyses were used, although small systematic off-sets occur between ICP-MS and ICP-AES data from the same samples. The ICP-MS analyses of diluted and undiluted runs were compared and seemed satisfactory for most trace elements. Rocks were analyzed for major elements by XRF at Wesleyan University and for trace elements (including the REE) by ICP-MS at SGS Minerals Services after fusion with sodium peroxide and dissolution of the resulting glass in acid (Varekamp et al., 2006).

Many 'hyper-acid' fluids (pH < 1) have H⁺ contents that cover a large range, and pH values are thus not a very suitable parameter to subdivide such fluids. Here the 'degree of neutralization' (DON) of these fluids, a semi-quantitative parameter that compares the measured or calculated acidity with the original H⁺ concentration based on its anion contents is used (Varekamp et al., 2000). The DON value is a reflection of the neutralization history of a fluid that acquired its acidity through absorption of volcanic gases. The DON value (in %) equals 100–{100 * [H⁺] (measured or calculated)/[H⁺] (original)} (see Varekamp et al., 2000 for further calculation details and approximations).

4. Chemistry of the Copahue volcanic acid fluids

4.1. General aspects

The acid Copahue-summit waters are acid Cl–SO₄ brines with high contents of the RFE and the volcanogenic elements, S and the halogens (Table 1) as well as a suite of volatile trace elements

such as Zn, Pb, Cu and As (Table 2). The fluids from the Copahue geothermal system (Las Machinitas, Las Machinas, Copahue village geothermal pools; described by Ouimette, 2000) are Cl-poor, SO₄-rich and mildly acidic, with modest amounts of RFE. These fluids are largely heated meteoric waters and are not further considered here. The concentrations of the individual RFE in the Copahue source fluids (Vertedero hot springs and crater lake – CP and CPL, respectively, in Fig. 1) range from 10 to 1000 s of mg/L (Table 1). The fluids have acquired these RFE through water–rock (W/R) interaction at depth, but despite the H⁺ consumption during this process have remained very acid. The DON value as defined before for these fluids ranges from 9% to 99%, indicating that some of these waters with high RFE concentrations are still relatively 'immature'. The 2000 CP spring waters that are associated with the eruptive period were closer to full neutralization and contained high concentrations of RFE, indicating enhanced W/R interaction between the hydrothermal fluids and a newly intruded magma (Varekamp et al., 2001). This higher level of maturity is also expressed in the mineral saturation characteristics of the CP spring fluids: the 1997–1999 waters were saturated with silica and gypsum/anhydrite, whereas the 2000 and later fluids were saturated with many more minerals, including jarosite, alunite and a suite of Al–silicate minerals (Varekamp et al., 2004).

The reservoir temperature of the system was derived from the S isotope equilibration between bisulfate and native S, and yields temperatures of 300–350 °C (Ouimette, 2000; Varekamp et al., 2004). The exact depth of the hydrothermal system is not known, but extrapolation of the liquid–vapor curve to ~300 °C suggests a minimum depth of about 1500 m for a single phase system. This would put the system within the roots of the modern Copahue volcano, which was built upon the older deposits of the Caviahue volcanoes that are exposed in the caldera walls (Varekamp et al., 2006). The potential protoliths for W/R interaction are most likely the basal Copahue rocks, for which compositions were reported in Varekamp et al. (2006).

The composition of Copahue crater lake differed in RFE from that of the Copahue hot springs before the 2000 eruption, but the two water types became much closer in composition after the lake had reformed in 2001 after the 2000 eruption. The RFE concentrations in both the crater lake and CP hot springs changed strongly with the eruption, e.g., the Mg concentrations went up while the K concentrations went down (Fig. 2a); the SO₄²⁻ concentrations dropped in both water types after the eruption, and continued to do so in the years following (Fig. 2b).

Table 1
pH and major element concentrations (μg/L) in Copahue (Vertedero) hot springs and crater lake by year.

Date	pH	F	Cl	SO ₄	Na	Mg	Al	P	K	Ca	Ti	Mn	Fe
<i>Hot springs</i>													
3/15/1997	0.4	nd	10,600	64,200	940	640	3870	64	790	1100	4.7	25	2190
3/20/1998	0.4	nd	10,200	64,000	1020	640	3690	51	930	1420	3.4	34	2270
1/06/1999	0.3	700	9800	65,400	910	500	3250	67	880	770	11.6	23	1860
11/26/1999	0.2	500	6800	45,400	520	300	1940	30	470	800	4.3	13	970
7/16/2000	0.8	700	8400	51,400	1500	1870	5320	53	710	610	17.6	54	2780
1/17/2001	2.4	230	4300	30,900	900	960	2950	50	660	710	3.8	34	1580
3/21/2002	1.5	1300	7800	24,500	1180	2830	1720	11	190	860	1.1	95	3590
1/18/2003	1.7	750	6600	11,100	1010	1870	1010	3	60	600	0.1	70	2140
3/14/2004	2.3	840	9800	15,600	1540	1720	2210	10	130	680	0.3	71	2610
11/23/2004	1.5	220	3800	8800	540	640	1020	5	120	630	0.3	23	780
<i>Crater lake</i>													
3/15/1997	0.3	960	10,300	64,200	790	490	2700	33	640	810	3.0	20	1320
3/20/1998	0.3	840	8600	59,600	590	370	2020	25	480	800	2.6	15	960
1/06/1999	0.3	720	8000	55,400	470	290	1560	20	390	850	3.2	13	800
11/26/1999	0.2	950	9100	66,000	430	270	1490	20	370	840	5.0	13	750
1/17/2001	1.1	230	4300	20,000	460	1830	360	2	50	450	0.7	50	1780
3/21/2002	0.6	740	9000	34,900	700	1430	1040	bd	80	680	1.6	48	2100
1/18/2003	0.6	970	14,500	31,700	1200	1470	2400	15	260	1020	2.7	52	1890
11/23/2004	0.8	520	6700	20,700	560	590	1190	11	170	900	1.5	22	760

Table 2Trace element data in $\mu\text{g/L}$ for Copahue hot springs samples over time; bd = below detection.

	3/15/1997	1/6/1999	11/26/1999	7/16/2000	1/17/2001	3/21/2002	1/18/2003	3/14/2004	11/23/2004
Ag	5	19	14	11	6	78	12	16	7
As	4520	10,980	6500	6900	4330	7250	4110	5830	2910
Ba	63	37	52	58	82	bd	bd	110	47
Cd	90	120	80	130	110	120	70	90	30
Co	80	320	160	1460	600	180	230	110	110
Cr	1540	2160	1090	6010	1750	750	330	710	520
Cs	69	90	54	97	83	62	33	53	18
Cu	170	530	220	750	730	440	120	40	140
Hf	0.9	7.5	12	0.9	1.8	2.6	1.1	0.6	0.2
Mo	2	3	2	7	3	bd	2	2	2
Nb	0.3	0.5	0.4	0.5	0.3	bd	0.3	0.2	bd
Ni	550	860	630	2800	1210	390	380	200	250
Pb	2290	3490	2200	1500	1900	1330	130	760	300
Rb	1750	2350	1300	2030	1820	1350	810	1440	540
Sc	720	860	530	980	750	810	430	790	290
Sn	7	100	60	20	8	20	1	4	1
Sr	15,400	21,000	14,300	17,100	16,500	9300	5700	6280	5870
Ta	0.3	0.4	0.2	0.3	0.2	bd	0.3	0.2	bd
Th	220	340	190	250	250	60	20	70	50
U	46	93	50	70	67	18	7	17	24
V	5250	6790	3910	8510	5590	5200	3230	4780	1880
Y	550	840	540	780	710	810	520	560	310
Zn	2450	2830	1860	4350	3200	10,100	4900	5120	1800
Zr	140	2270	1650	320	390	160	40	10	6

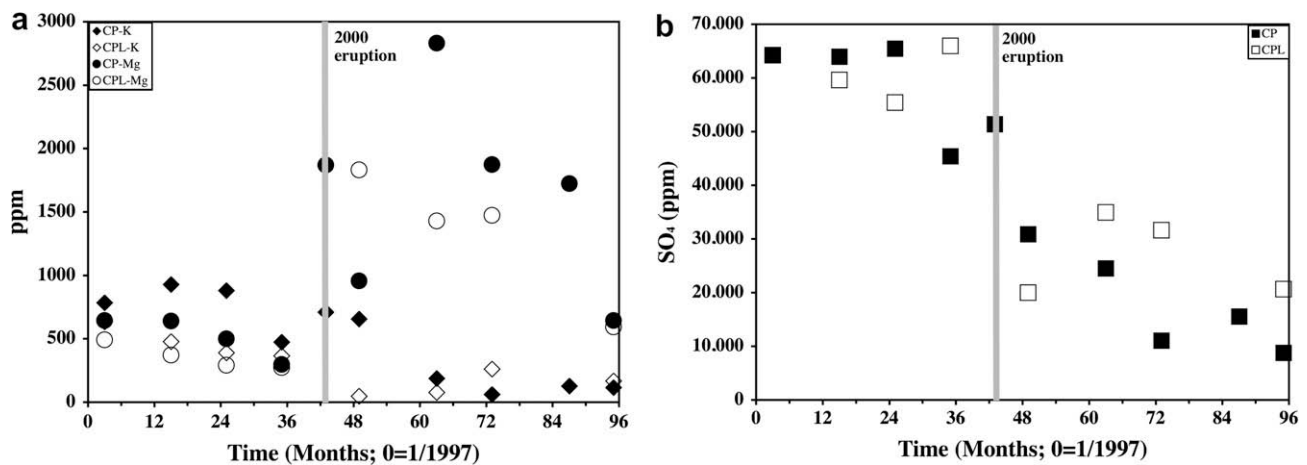


Fig. 2. Compositions of Copahue hot spring (CP) fluids and Copahue crater lake (CPL) over time. (a) Change in K and Mg concentrations before and after the 2000 eruption, and a decrease in the difference between the two water types after the eruption. (b) Decrease in SO_4 concentration in CP and CPL waters after the 2000 eruption and in the years following.

The elemental concentrations in the URA and Lake Caviahue waters varied over the 8-year period, a result of variations in the composition and discharge rate of the CP source springs and the dilution with glacial meltwater. The Lake Caviahue water composition is driven by the input compositions and flow rates of the URA, the Agua Dulce (R. Dulce in Fig. 1), and direct precipitation as well as by the compositional momentum of the vast volume of lake waters (non-steady state effects). The evolving composition of Lake Caviahue waters provides insight into the mean secular trends in element fluxes, which complement the once a year spot samples from the URA (Varekamp, 2008). The URA element concentrations near the entrance of Lake Caviahue are diluted versions of the concentrated Copahue main spring fluids (CP), slightly modified by several near-neutral, concentrated tributaries on the mountain (Ouimette, 2000).

4.2. Major element variations

The Cl, F and SO_4 concentrations in the springs, rivers and lakes are largely a function of the concentration of these substances in

the source fluids, the flow rates of the springs and the degrees of dilution with meltwater. Fluoride probably behaves perfectly conservatively (as shown by Gammons et al., 2005), whereas Cl should be close to conservative as well. Small fractions of SO_4 are precipitated in gypsum and jarosite (URA) or reduced to sulfide in the Lake Caviahue bottom sediment (Koschorreck et al., 2008).

Secular trends in the hot spring and crater lake RFE compositions before the 2000 eruptions show low pH values with high concentrations of Al, K, Ca, Ti and P. These elements drop significantly in concentration after the 2000 eruptions; the pH values rose in the CP fluids, whereas the crater lake remained very acidic. The Mg and Mn concentrations increased during and after the eruptions (Varekamp et al., 2001), whereas the Fe concentrations show no clear time trends. The Mg concentrations in the hot spring fluids are a direct reflection of the W/R interactions in the hydrothermal system, as no Mg-bearing minerals precipitate at these low pH values at any of the observed or calculated temperatures. Element fractionations in the URA, Lake Caviahue or further downstream as a result of non-conservative behavior during travel through the landscape (Verplanck et al., 2004; see Gammons et al., 2005

for a detailed discussion of the LRA) are not considered further, but the focus here is mainly on the Copahue acid springs, URA and the crater lake.

To assess the W/R interaction process, element ratio plots and rock-normalized diagrams for the CP fluids are presented. These diagrams distinguish between pre- and post-2000 eruption rocks and fluids, assuming that the compositional changes in the fluids during the eruption were related to W/R interaction processes between fluids and the magmatic rocks in the hydrothermal reservoir (Varekamp et al., 2001). The Copahue rocks (<0.8 Ma) are mainly basaltic andesites, with the 2000 magma a relatively mafic olivine – clinopyroxene – plagioclase bearing rock (Varekamp et al., 2006). The underlying Caviahue sequence (>2.0 Ma) has a much wider compositional range, from basaltic andesites to rhyolites. A dacite from the Caviahue caldera wall is used as an example of an evolved rock from the Caviahue series (Varekamp et al., 2006).

The pre-eruptive CP fluids have Mg/K and Mg/Al values that overlap with those of the more evolved pre-eruptive Copahue rocks, but plot well away from the Caviahue dacite (Fig. 3a). The post-eruptive fluids plot towards much more Mg-rich compositions, some compatible with element ratios in the 2000 magma, but also many fluids with higher Mg/element ratios than those found in the rocks. The fluids plot on an approximately linear trend with Mg/K up to 30 (Fig. 3a). The Mg/K versus Na/Al plot shows a similar pattern (Fig. 3b), but the Caviahue dacite now plots well away from the array of Copahue rocks and fluids. Once more, the post-2000 fluids are more Na- and Mg-rich, plotting at much higher element ratios than the rocks.

These binary diagrams and many others suggest that the rock protolith for W/R interaction is most likely a stack of basal Copahue lavas or mafic lavas from the Caviahue series, which are common at the top of that sequence (Varekamp et al., 2006). The more evolved members (dacites/rhyolites) of the underlying Caviahue sequence are very unlikely protoliths. Lead isotope studies of the CP fluids indicated beyond doubt that the Pb in the Copahue spring fluids was derived from the Copahue magmatic system and not from Pb leaching from the older Caviahue rocks (Varekamp et al., 2006). In the following discussion, therefore a compositional average of 15 Copahue rocks is used as the hypothetical rock matrix for pre-2000 fluids and an average of six rock analyses of the 2000 magma for the post-2000 fluids.

A comparison of element patterns in the pre-eruptive and post-eruptive CP fluids through simple normalization to the rock protoliths shows that the pre-2000 fluids are depleted in Mg, Na, Ca and Ti compared to Fe, Al, K and P. The Ca-depletion is most likely a re-

sult of gypsum/anhydrite precipitation, and the Ti depletion may be the result of its poor aqueous mobility. The Mg–Na depletion may reflect the maturity of the protolith: the most easily leached elements Mg and Na (in olivine and plagioclase) had already been largely removed during earlier W/R interaction. The 2000 fluids show a strong enrichment in Al, Mg and Na, whereas the other elements remained roughly similar in relative enrichment. Subsequently, the degree of Mg enrichment increases, to fall again in 2004. Depletions in Al and K develop in the post-eruptive period, most likely the result of alunite precipitation in the deep system and near surface environment. The CP fluids are also severely depleted in Si, which is probably precipitated as hydrothermal silica in the hydrothermal reservoir (Varekamp et al., 2004).

An alternative approach to simple rock normalization is the use of element transfer ratios (ETR), as first introduced by Pasternack and Varekamp (1994). The ETR approach uses a normalization factor created by dividing the concentration of an “easily dissolved element” (e.g., a highly incompatible element such as Cs that forms no secondary minerals) in the fluids by the concentration of that element in the unaltered rock protolith. The element concentrations of the rocks are then multiplied with that normalization factor which creates a set of “predicted” element concentrations in a fluid if congruent rock dissolution had occurred, and no precipitation of secondary phases was involved. The ETR are then obtained by dividing the measured concentrations over these predicted concentrations (multiplied by 1000 to obtain numbers >1). Such ETR diagrams thus show the combined effects of secondary mineral precipitation as well as non-congruent rock dissolution behavior, with ETR values of one indicating simple congruent rock dissolution. A Cs-based ETR diagram for pre-eruptive CP fluids (Fig. 4a) shows strong relative depletions in Ti, a slight dip in Mg, Ca and Mn, but highs in K and P. These ETR values decrease over time, possibly indicating the progressive exhaustion in reactive minerals before the 2000 eruption. During the post-eruptive period, the initial fluids (2000, 2001) show modest ETR values just above one for Fe, Al, Mg, Na, K and P, but depletions in Ca and Ti (Fig. 4b). Over time, significant peaks in ETR develop for Mg and Na, with a lesser peak in Fe, whereas Al, K and P decrease. In early 2004, the first sign of protolith maturation and exhaustion appears again with decreased Mg ETRs.

4.3. Trace elements

Trace element data of the CP hot springs show a wide range but almost all elements are very high in concentration compared to

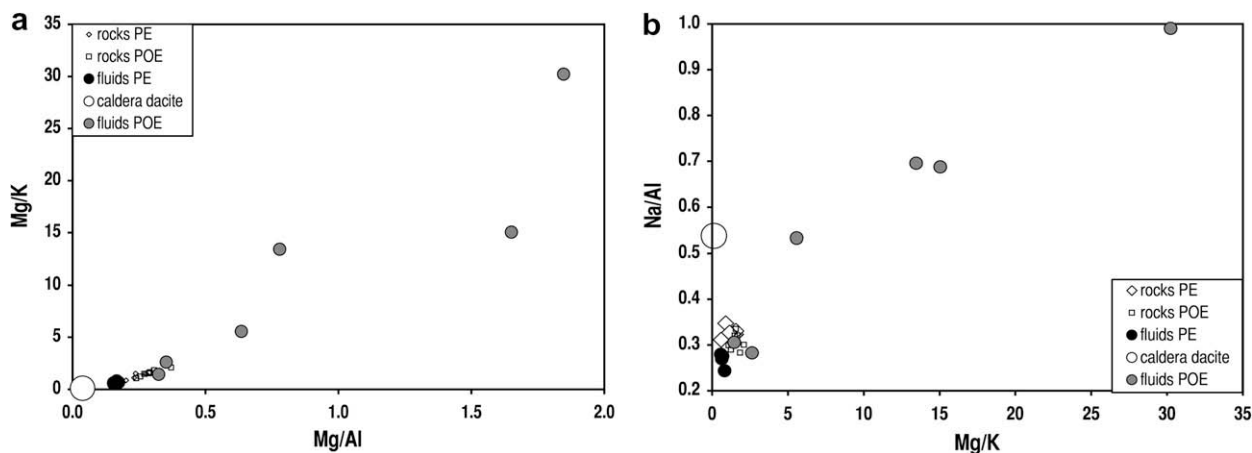


Fig. 3. Element ratio (weight) plots of Copahue fluids with pre-eruptive Copahue rocks and fluids (PE), post-eruptive rocks and fluids (POE) and a dacite from the older Caviahue caldera series. (a) Mg/Al versus Mg/K. (b) Mg/K versus Na/Al.

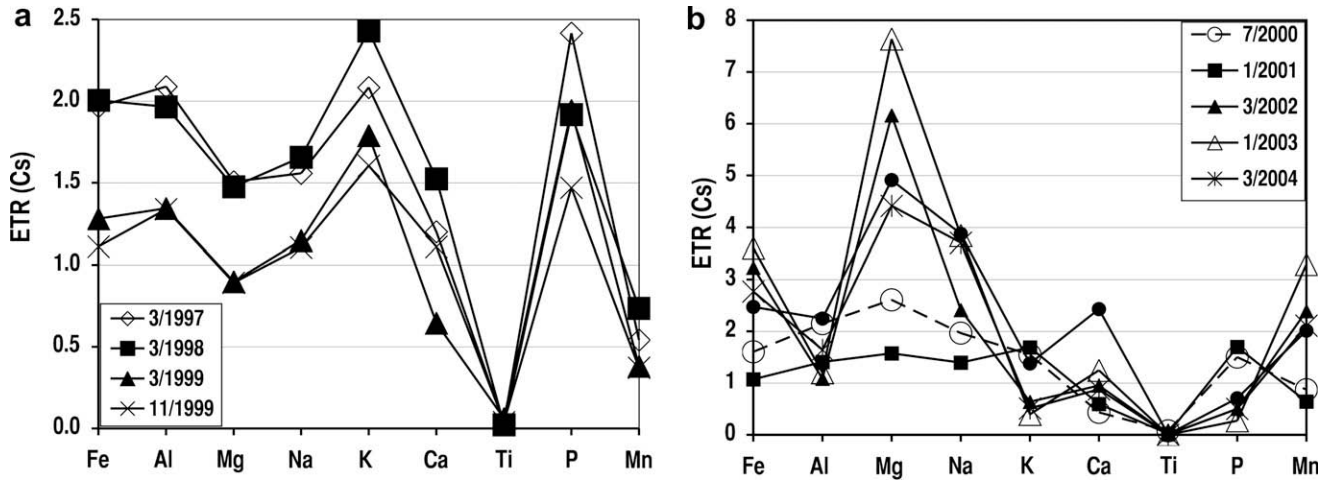


Fig. 4. Element transfer ratio (ETR) diagrams based on Cs for pre-eruptive fluids (a) and for post-eruptive fluids (b). Note strong depletions in Ti in both diagrams, the high ETR values for Mg and Na and the low ETR values for Al and K in the post-eruptive fluids.

non-volcanic surface waters (Tables 2 and 3). Secular trends in trace elements show very high concentrations in the 1999 samples, and an overall drop off in concentrations in the CP fluids after the eruptions. Some toxic elements are present in very high concentrations in the CP spring fluids, with maximum values of 11 mg/L, As, 0.7 mg/L, Cu, 3.6 mg/L B, 3.5 mg/L Pb, 1.3 mg/L Ti, 2.8 mg/L Ni, 0.13 mg/L Cd and up to 6 mg/L Cr. The URA near the entrance of Lake Caviahué is more dilute, with maximum values of 640 µg/L As, 140 µg/L Cu, 370 µg/L B and 200 µg/L Ni. Copahué is a significant source of toxic trace elements to the lake and the local environment.

Trace element Cs-based ETR diagrams (Fig. 5) show extreme depletions in both pre- and post-eruptive CP fluids in Ta, Nb, Zr and Hf. Strong negative anomalies also occur for Ba, Co, Cu, Sn and Mo, whereas Sr and Rb show slight enrichments in post-eruptive fluids. The ETR values of U and Th are close to one for the pre-eruptive fluids, but slightly below one for post-eruptive fluids. The U/Th values in the fluids and local Copahué rocks are very similar (Fig. 6). The REE as a group hover at ETR values just below one for the pre-eruptive fluids, whereas the heavy rare earth elements (HREE) are enriched in the post-eruptive fluids. The ETRs of the compatible elements Y, Sc, V, Ni and Cr are well above one, whereas Co has much lower ETR values. The chalcophile elements Zn and Pb show strong enrichments, especially in the post-eruptive fluids, whereas Cu is strongly depleted in both. The Cd concentrations correlate positively with the HREE (as was documented also for mean-ocean-ridge basalt glasses by Yi et al. (2000), suggesting derivation from the rock matrix of these elements and no strong Cd source in the volcanic vapors.

Variations in REE concentrations (Table 3) in CP fluids over time are shown first in chondrite-normalized relative abundance dia-

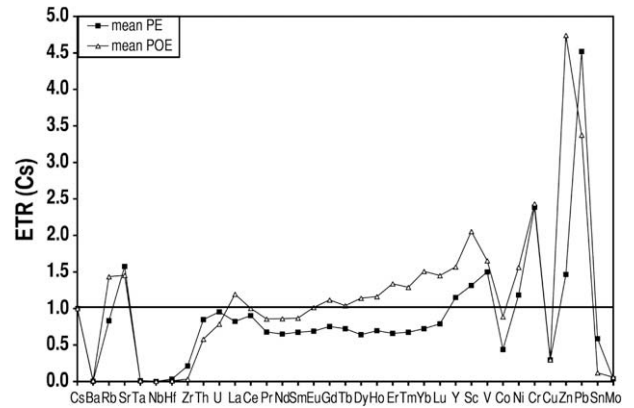


Fig. 5. Element transfer ratio (ETR) diagram based on Cs for trace elements in pre- and post-eruptive fluids. Note strong depletions in the HFSE, Ba, Co, Cu, Sn and Mo, but enrichments in post-eruptive fluids in HREE. The ETR of Y, Ni, Cr, Sc, V are in excess of one, probably the result of dissolution of phases associated with olivine. The ETRs of Pb and Zn are very large, probably indicating volcanic gas derived element inputs.

grams. All pre-2000 CP water samples are light rare earth element (LREE) enriched relative to the Copahué rocks (Fig. 7a). The 2000 fluid samples have slightly steeper LREE slopes than Copahué rock (Fig. 7b), but as in the pre-2000 fluids, middle rare earth elements (MREE) and HREE have slopes that are broadly similar to that of rock. In 2001–2002, LREE enrichment is still pronounced in the fluids, which decreases in the 2002 samples. Most striking are the LREE patterns of the 2003–2004 samples, which are similar to that

Table 3
Rare earth element concentrations (µg/L) in Copahué hot springs by year; bd = below detection.

Date	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
3/15/1997	590	1280	140	540	110	26	110	14	90	17	53	8	54	8
1/6/1999	1080	2140	220	850	170	43	180	23	140	28	85	12	84	12
11/26/1999	640	1370	150	590	120	29	120	16	90	18	53	7	50	7
7/16/2000	590	1270	140	550	110	34	130	18	120	24	77	11	78	12
1/17/2001	880	1750	180	690	140	35	140	20	120	23	71	10	69	10
3/21/2002	660	960	100	400	90	23	110	18	110	23	81	10	83	bd
1/18/2003	400	550	60	240	50	16	70	10	70	15	50	8	54	9
3/14/2004	350	510	50	220	50	16	70	10	70	15	52	8	63	10
11/23/2004	220	470	60	260	60	17	60	9	50	10	30	4	29	4

of the mean rocks but show some HREE enrichment. Many fluid samples show strong La enrichment relative to the other LREE (Fig. 7b).

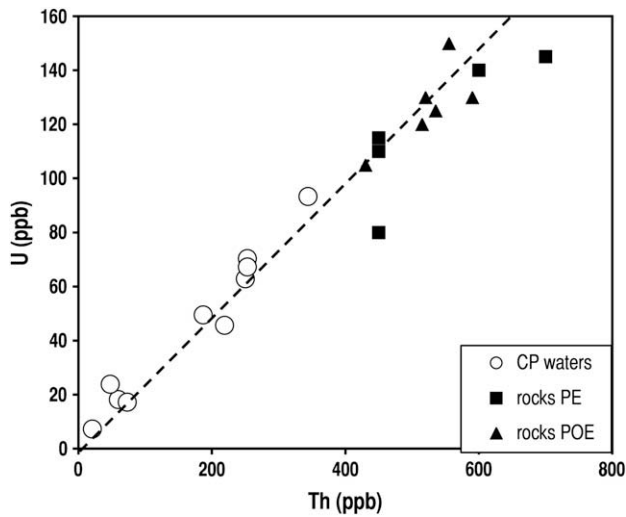


Fig. 6. The concentrations of U and Th in fluids and rocks from Copahue. The uniform U/Th in fluids and rocks suggest similar mobilities for these two elements in acid fluids.

A more detailed view of REE patterns over time is shown in a rock-normalized REE diagram (Fig. 8), where horizontal fluid-REE patterns represent those similar to rocks. Pre-eruptive samples show enrichments in the LREE (especially La, Ce), whereas the 2000 samples show only slight LREE enrichments but some HREE enrichment. The 2002–2004 samples show the most fractionated

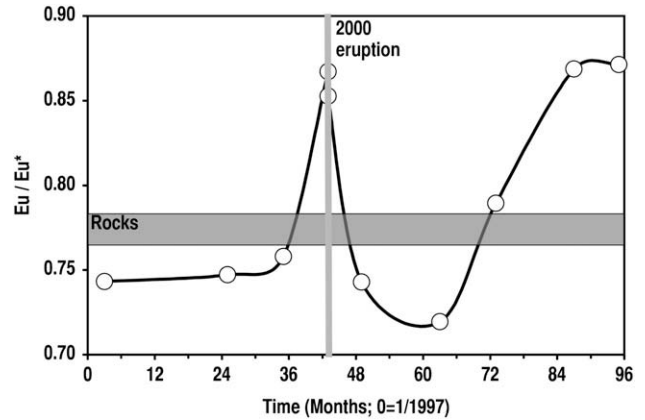


Fig. 9. The magnitude of the Eu anomaly varied over time in the Copahue CP fluids. Note the increase in Eu/Eu^* during the 2000 eruption and in 2004. Shaded area is the range of Eu anomalies in the Copahue rocks.

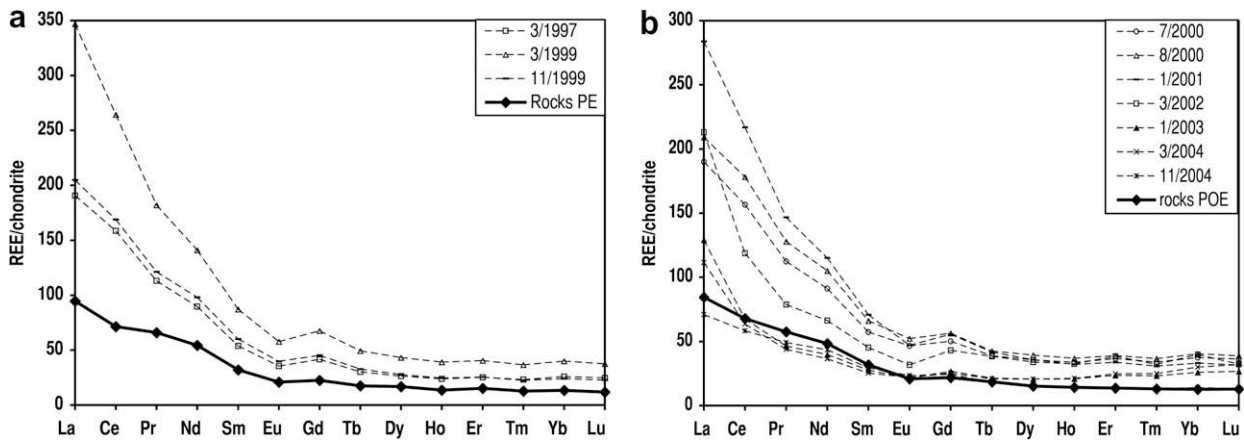


Fig. 7. Chondrite-normalized REE patterns for pre- (a) and post-eruptive fluids (b), and rocks. All pre-eruptive fluids are LREE enriched relative to the mean rock protolith, whereas the post-eruptive rocks show much more variations.

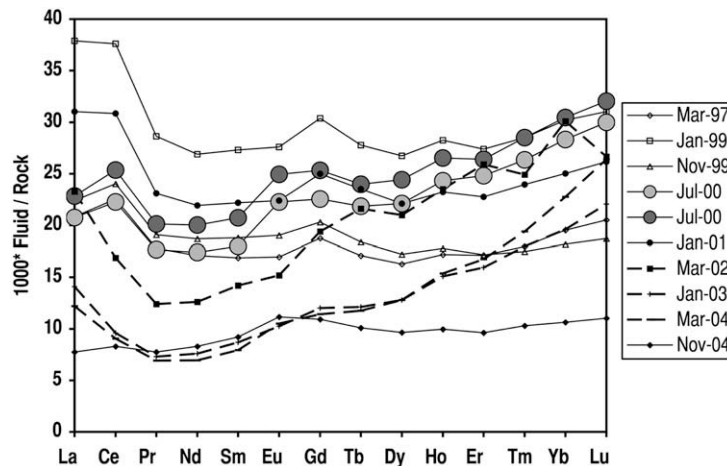


Fig. 8. Rock-normalized REE diagram for all Copahue hot spring fluids.

patterns with LREE and HREE enrichment (or depletions in MREE). The November 2004 sample shows the anomalous flat pattern similar to bulk rock. Most of these acid fluids have small negative Eu anomalies, defined as the chondrite-normalized Eu concentration divided by the Eu value obtained from the mean of the chondrite-normalized Sm and Gd concentrations (Eu^*). The Eu/Eu^* values show clear shifts over time, with the highest values (closest to 1) during the 2000 eruption and in 2004 (Fig. 9).

Table 4

pH and major element concentrations (mg/L) by year for Lake Caviahue (N, north arm; S, south arm); *m* is water depth in meters; nd = not determined.

Date	Arm	<i>m</i>	pH	F	Cl	SO ₄	Na	Mg	Al	K	Ca	Fe
3/14/1997	N	10	2.5	10	88	340	13	14	29	6	20	19
3/14/1997	N	60	2.5	nd	85	340	13	13	27	6	19	18
3/18/1997	N	20	2.4	11	82	330	11	14	28	6	19	18
3/18/1997	S	40	2.6	11	81	320	10	13	25	5	18	17
3/19/1998	N	0	2.3	nd	85	370	13	14	29	7	20	18
1/8/1999	S	30	2.5	11	91	470	13	14	30	7	20	20
1/8/1999	S	50	2.4	10	92	440	13	14	30	7	20	20
1/11/1999	N	70	2.4	10	92	460	14	15	32	7	21	21
11/23/1999	S	70	2.4	10	99	480	13	15	34	8	23	22
11/23/1999	S	20	2.4	10	94	470	12	15	32	8	22	21
11/23/1999	N	30	2.2	nd	90	460	11	14	31	7	22	20
7/6/2000	N	70	2.1	12	117	710	16	24	36	8	28	35
7/6/2000	N	75	2.3	11	106	570	14	16	31	8	23	23
7/6/2000	S	0	2.2	9	104	480	12	14	26	8	22	19
1/15/2001	S	70	2.4	9	94	500	13	18	30	7	23	21
1/15/2001	S	30	2.3	9	91	490	13	18	30	7	24	21
1/15/2001	S	10	2.3	9	91	480	13	18	30	7	23	21
1/16/2001	N	50	2.4	9	92	500	13	18	30	7	24	22
3/20/2002	N	11	2.4	9	79	430	13	21	23	6	23	23
3/20/2002	N	75	2.5	8	82	450	13	20	27	6	23	23
3/20/2002	S	28	2.4	8	78	440	13	20	26	6	23	22
3/20/2002	S	63	2.5	8	78	480	13	20	30	6	22	22
1/22/2003	N	75	2.5	8	71	400	13	19	23	6	20	22
1/22/2003	N	20	2.5	7	71	350	13	20	22	5	18	20
1/23/2003	S	40	2.6	7	72	360	13	19	24	6	20	21
1/23/2003	S	20	2.4	7	71	330	14	19	22	5	20	21
1/23/2003	S	60	2.7	7	72	410	13	18	23	5	20	20
3/12/2004	N	20	2.3	9	86	350	14	24	23	5	20	23
3/12/2004	N	40	2.4	8	76	330	15	22	21	5	22	22
11/21/2004	N	0	2.6	8	80	330	15	22	22	5	20	22

Table 5

Trace element concentrations (μg/L) by year for Lake Caviahue (N, north arm; S, south arm) and the Lower Rio Agrio (LRA); *m* is water depth in meters; blank = below detection; nd = not determined.

Date	Arm	<i>m</i>	Mn	P	Sr	Sc	Ti	V	Ni	Cu	Zn	Cr	Co	As	Y	Ba	B
3/01/1997	N	0	810	910	200	5	100	60	10	13	6	10	10		12	15	130
1/12/1999	S	60	810	400	190	5	120	50	13	17	54	16			10	13	36
1/12/1999	N	80	850	470	210	5	130	60	13	13	54	16		35	10	13	42
11/23/1999	N	80	830	420	210	5	150	60	20	24	147	16		33	10	50	54
11/23/1999	S	70	850	480	210	5	150	60	34	70	165	22		36	11	48	56
7/06/2000	N	80	1090	530	280	7	200	90	37	63	99	27	18	39	14	20	39
7/06/2000	S	0	740	370	210	5	140	50		13	39	10			7	10	
1/15/2001	S	60	900	480	230	5	150	60	19	23	49	17	10	36	11	15	28
1/16/2001	N	75	940	480	220	5	150	60	23	13	49	18	12	40	11	16	30
3/20/2002	N	60	950	420	200	4	120	50	24	20	129	15	12		11	52	57
3/20/2002	S	60	890	410	190	4	120	60	23	21	126	15	11		11	56	56
1/22/2003	N	75	960	260	170	4	100	50	47	19	135	13	11		10	78	55
1/22/2003	N	30	910	260	160	3	90	40	20	33	209				7	60	nd
1/22/2003	N	40	910	290	170	4	90	40	20	36	257			30	7	70	nd
1/22/2003	N	75	910	260	160	4	110	40	40	24	143	10			7	40	nd
1/23/2003	S	60	920	310	170	3	90	50	23	19	113	12	11		10	76	48
1/23/2003	S	72	880	190	170	5	180	50	30	55	227	10			7	30	nd
1/23/2003	S	60	840	320	160	4	90	50	20	26	122	10			8	80	nd
1/23/2003	S	10	980	270	190	4	100	40	20	17	119				7	70	nd
1/23/2003	S	0	920	280	170	3	90	40	10	11	107		10		7	70	nd
3/12/2004	N	10	1060	240	160	4	70	40	20	6	61			30	10	10	nd
3/12/2004	N	50	950	240	150	3	70	40	10	9	54				9	10	nd
11/21/2004	N	0	1020	220	160	4	60	40	20	9	57				9		nd
8/12/2000	LRA	0	420	180	120	3	70	30		17	22						nd
3/13/2004	LRA	0	1060	220	170	4	70	40	20		63				10		nd
11/23/2004	LRA	0	890	170	140	3	60	30	10	10	49				8		nd

5. The composition of Lake Caviahue and element fluxes through the Upper Rio Agrio

The secular variations in fluid compositions discussed above were largely based on annual samples of the CP hot springs. The time trends in the chemical composition of Lake Caviahue are driven by variations in the element input rates of the URA, and provide an average of these secular trends in URA element fluxes. Lake Caviahue is a large lake (~0.5 km³ water) of glacial origin, fed by the acid URA and the meltwater stream Agua Dulce (Delpino et al., 1997; Varekamp, 2003). Direct precipitation, seepage and evaporation also impact the water budget of the lake, which has an overflow at the NE side of the northern arm, feeding the LRA. The composition of the lake waters (selected data in Tables 4 and 5, complete data in Varekamp, 2008) has varied over the 8-year observation period, with pH ranging from 2.1 to 2.7 and varying RFE concentrations of Al (25–36 mg/L), Mg (13–24 mg/L), Fe (15–35 mg/L), K (5–9 mg/L) and volcanogenic element concentrations of Cl (70–118 mg/L), F (7–12 mg/L) and SO₄ (325–730 mg/L). Some toxic trace elements (Table 5) have relatively high concentrations (maximum values listed) in the lake: As (40 μg/L), Ni (47 μg/L), Cu (109 μg/L), Zn (257 μg/L), and B (130 μg/L), but nonetheless, the lake has substantial organic productivity, with P concentrations up to 910 μg/L (Pedrozo et al., 2001, 2008; Wendt-Potthoff and Koschorreck, 2002).

The elemental influxes into Lake Caviahue were determined from measured URA water fluxes and the river water composition (Varekamp, 2008; Tables 6–8). The magnitude of these element fluxes are dominantly a function of the flow rate of the CP source springs and their composition; for several elements no simple correlation exists between CP fluid compositions and URA element fluxes as determined at the entrance of Lake Caviahue. The hot spring flow rates are probably the more important variable in determining the element flux rates. The compositional trends in the waters of Lake Caviahue (Fig. 10) show that this acid lake was most concentrated in 2000 during the eruptive period, with a period of strong dilution directly following the eruptive events (2001, months 48–60). During the period 2002–2003 (months

Table 6

Major element concentrations (mg/L) of the Upper Rio Agrio at the bridge in Caviahue over time; nd = not determined.

Date	F	Cl	SO4	Na	Mg	Al	K	Ca	Si	Fe	Mn	P
1/07/1999	46	950	4740	100	100	280	65	170	36	170	6	5.7
11/25/1999	15	180	1060	24	25	55	14	49	15	31	2	1.0
7/06/2000	21	130	1220	33	130	76	7	88	nd	130	4	0.7
1/13/2001	11	120	790	27	58	45	9	72	23	34	3	0.1
3/24/2002	36	280	1170	26	71	44	5	45	19	53	3	0.1
1/21/2003	17	170	460	30	62	27	6	44	20	23	3	bd
3/12/2004	120	1490	2790	210	310	260	34	160	nd	320	12	1.9
11/22/2004	11	180	560	28	40	41	6	36	nd	32	2	0.3

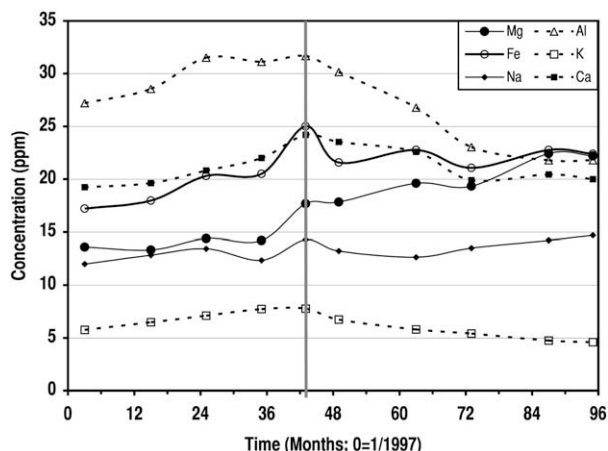
Table 7Trace element concentrations ($\mu\text{g/L}$, collected by ICP-AES) of the Upper Rio Agrio at the bridge in Caviahue over time; bd = below detection; nd = not determined.

Date	Sr	Sc	Ti	V	Ni	Cu	Zn	Cr	Co	As	Y	B
1/07/1999	1830	60	1550	580	120	50	310	170	50	460	89	370
11/25/1999	410	10	270	110	30	10	160	30	10	90	21	100
7/06/2000	590	20	310	200	200	140	260	100	110	40	42	nd
1/13/2001	360	8	60	70	90	110	120	20	60	bd	30	87
3/24/2002	340	7	50	80	50	30	260	10	30	52	32	91
1/21/2003	270	5	bd	bd	30	10	130	bd	20	bd	20	55
3/11/2004	1200	70	170	600	80	30	850	100	50	640	90	nd
11/22/2004	260	8	40	70	20	10	90	20	bd	70	16	nd

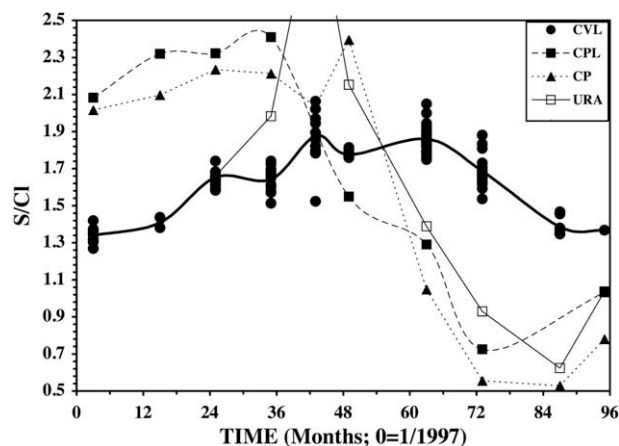
Table 8

Pre-eruptive element fluxes (1999; PE) and the mean post-eruptive fluxes (2001–2004; POE); values are in kilotonnes/a, except As and B (tonne/a).

	F	Cl	S	Na	Mg	Al	K	Ca	Fe	Si	As	B
PE	0.9	14	25	1.6	1.7	4.2	1.0	3.1	2.5	0.8	6.8	6.4
POE	1.0	11	12	1.7	3.3	2.1	0.3	2.5	2.0	0.8	2.7	3.6

**Fig. 10.** Average compositional trends in Lake Caviahue waters with time, reflecting changes in the input strength of the Upper Rio Agrio into the lake that reflect compositional changes and flow rates of the summit hot springs (CP). Horizontal scale in 'months' starting in January 1997 and ending in December 2004; eruption took place in month 43, July 2000. Elements that decreased in concentration after the 2000 eruption (Al, Ca, K) are shown with dashed lines.

60–84) the dilution in Al Ca and K continued, whereas the Na and Mg concentrations gently increased. The years 2003–2004 (months 84–96) saw a pause in the dilution of Al and stronger increases in Mg and Na concentrations. The overall lake dilution continued however during 2006 (Varekamp, 2008). The S/Cl values in the Copahue hot springs varied over the 8-year period, with a decrease in S/Cl after the eruption (Fig. 11). The S/Cl in Lake Caviahue waters trail those in the URA input (and those in the CP and CPL waters) because of non-steady state effects.

**Fig. 11.** The S/Cl values in the Caviahue lake waters, the Copahue hot springs and crater lake and the URA before entry into Lake Caviahue. The data show the decrease in S/Cl after the 2000 eruption, and that the CP, CPL and URA samples lead the CVL compositions. The S/Cl value recovers at the end of 2004, suggesting enhanced S inputs into the system possibly associated with new magmatic activity. Horizontal axis as in Fig. 10.

Most elements behave pseudo-conservatively in the lake, with minor sinks for SO_4 (SO_4 reduction and pyrite formation in sediment) and P (take-up during primary organic productivity). The elements are exported from the lake through the LRA, where bright yellow–orange–brown hydrous Fe-oxides started to precipitate at the 'Salto di Agrio' (large waterfall in the LRA) past the confluence with the neutral Trollope river in 2003 (Fig. 1). This 'front of Fe-rich mineral precipitation' has moved from the Salto area towards the lake outlet as a result of the ongoing dilution of the lake waters and increase in pH, and was near to the lake outlet in 2008.

6. Discussion

The compositional variations of the Copahue fluids (CP and CPL samples) and the evolution of Lake Caviahue over time largely reflect W/R interaction processes at depth and fluctuations in discharge rate from the deep system. Factors that play an important role are:

1. the dissolution kinetics of glass and minerals, e.g., plagioclase and olivine react rapidly with the hot acids,
2. the maturity of the rock protolith, resulting from earlier acid dissolution,
3. the availability of ligands to complex the dissolved elements,
4. the precipitation of secondary minerals as a function of P, T, fO₂ and element speciation.

In addition, changes in the volcanic volatile element fluxes impact the concentrations of volatile major and trace elements in the hot spring waters. The composition of the hot spring and crater lake fluids is fractionated relative to the rock protolith as a result of all these factors and processes. The waters change composition further downstream in the rivers and lakes as a result of dilution, precipitation of new minerals and adsorption-desorption reactions. The zone directly downstream of the hot springs at the Copahue summit is covered with fresh red hematite and gypsum precipitates, and there is spectral evidence for the presence of jarosite (Varekamp, 2004). At the outflow of Lake Caviahue and in the LRA, abundant precipitates of Fe-rich minerals have formed since 2003 and are still forming today. These surficial processes are discussed in detail by Gammons et al. (2005) and Parker et al. (2008).

The elements F, Cl, Mg and Na do not form secondary phases during cooling/neutralization of these fluids, but Ca, Al, K, Fe and SO₄/S²⁻ may have formed minerals such as anhydrite, barite, jarosite, alunite and sulfides (according to saturation calculations of Varekamp et al., 2004). The temporal variations in these element concentrations may thus be related to mineral precipitation, changes in the rock dissolution process, or maturation of the protoliths. The Mg and Na compositional variations in the hot springs probably reflect changes in the latter two parameters only. Between early 1997 and late 1999, the CP fluids had relatively low Na and Mg concentrations and a very low pH. This is interpreted as the result of W/R interaction with a mature rock protolith: a low rate of element release and a low DON parameter for the fluids. At the same time, Lake Caviahue saw declining element input fluxes (Varekamp, 2008), but because the lake had not yet reached steady state with respect to most elements, it still became more concentrated during this period (Fig. 10). A sudden increase in element concentrations in CP fluids and in the URA fluxes of Na and Mg in mid-2000 strongly suggests the arrival and acid attack of new magma in the hydrothermal system at that time. This concentration spike is rapidly followed by the first eruptions, but in 2001 the hydrothermal system seems to have almost 'shut off'. The sudden decrease in element fluxes into Lake Caviahue in 2001 may have been caused by decreased permeability in the volcano-hydrothermal system, with precipitation of several new secondary minerals in the reservoir rocks. The hot springs became more dilute (Table 1), and Lake Caviahue in response also became more dilute (Fig. 10). The years 2001–2006 saw a general decline in element concentrations in Lake Caviahue, indicating diminishing element fluxes into the lake system. The element fluxes temporarily increased in 2004, possibly suggesting a new small intrusion of magma but no eruption (a 'failed eruption?'). The CP fluid concentrations show highly variable element concentrations post 2001: the concentrations of K, Al, Ca and S show an unsteady decline, probably related to both precipitation of jarosite–alunite–anhydrite in the reservoir at depth as well as depletion of the protolith in K and Al.

Most incompatible elements in fluids show rock-like relative abundance patterns, possibly the result of the dissolution of glassy, chilled magma which would be the main host of these elements. The negative Ba anomaly indicates barite precipitation, whereas the negative anomalies of Co, Mo, Sn and Cu suggest the formation of sulfides or oxides such as cassiterite and molybdenite. The high

field strength elements Ta, Nb, Hf, and Zr are almost immobile in these hot acid brines, creating depleted patterns in rock-normalized diagrams (Fig. 5); in mature protoliths, Zr seems more mobile than Ta–Nb–Hf. The protolith residue is presumably enriched in this group of immobile elements. The Copahue data suggest that Th is only slightly less mobile than U in the hot acid fluids. The elements Zn and Pb probably are present in excess with respect to the rocks, and are likely supplied by the volcanic gases. The compatible trace elements Ni, Cr and Co correlate with Mg in the pre-eruptive fluids, and are enriched in the syn-eruptive fluids, similar to Mg, probably the result of olivine dissolution. The Mg enrichments in the CP fluids during the post-eruptive period are not accompanied by enrichments in Ni–Cr–Co, suggesting mineral Mg sources other than olivine.

Rock-normalized REE patterns (Fig. 5) show a close to congruent REE removal from the rock matrix, but in detail, fractionations are present. Gammons et al. (2005) suggested that the REE distribution in the Copahue hot spring fluids may have varied over time. During W/R interaction, REE fractionations between bulk rock and fluid may occur as a result of the preferential dissolution of minerals with fractionated REE relative to the whole rock or the more incompatible LREE are released into the acid water prior to the more compatible HREE. For example, a study of the El Chichón andesites (Luhr et al., 1984) showed that plagioclase has strong LREE enrichments, a positive Eu anomaly, but low overall REE abundances, whereas other mineral phases have smaller LREE enrichments, negative Eu anomalies, but higher overall REE concentrations. The El Chichón anhydrite has strong LREE enrichments and is rich in REE, similar to hydrothermal anhydrite (Morgan and Wandless, 1980). The fine-grained groundmass or volcanic glass probably has the highest REE abundances with a REE pattern close to that of the bulk rock. The maturity of the protolith also will impact the fluid REE patterns (e.g., Michard, 1989; Kikawada et al., 1993, 2001; Bach and Irber, 1998; Fulignato et al., 1999; Sriwana et al., 2000; Takano et al., 2004), with already partially dissolved rocks providing possibly HREE enriched fluids during W/R interaction (LREE removed during earlier W/R interaction stage). It is unlikely that ligand preferences caused severe REE fractionations in these Cl- and SO₄-rich waters (Gammons and Li, 2002; Bozau et al., 2004). Precipitation or dissolution of REE-bearing secondary phases may further fractionate the REE in the water, with anhydrite/gypsum formation as an important process depleting the fluids in LREE.

The REE data from the Copahue hot spring fluids show that all pre-eruptive fluids are LREE-enriched with respect to the source rocks. During the 2000 eruptions and in late 2004, the fluids became more rock-like in their LREE pattern, but between 2001 and early 2004, the REE patterns were largely MREE depleted. The Eu/Eu* values increased during 2000 and late 2004 (Fig. 9), and were well above the Eu/Eu* of the bulk rock. These REE fractionations are interpreted as the result of the intrusion of new magma into the hydrothermal system in early 2000 (prior/during the eruption) and possibly during late 2004, with preferential dissolution of fresh plagioclase, which has a positive Eu anomaly (Eu/Eu* > 1), and possibly dissolution of chilled glassy rocks (close to bulk rock REE pattern). The HREE enrichments in the fluids from 2001 to 2004 may be related to protolith maturation.

Despite the acid conditions and relatively high levels of toxic elements, aquatic life is omni-present in these fluids, both in the hyperacid rivers and in the mildly acid Lake Caviahue (Wendt-Potthoff and Koschorreck, 2002; Pedrozo et al., 2001, 2008). The ecosystem in this lake is stimulated by the volcanic P input, which remains in solution until a pH > 3 is reached when it may become largely scavenged by Fe-rich minerals. As a result of the copious P input, Lake Caviahue is N-limited in its primary productivity (Pedrozo et al., 2008).

The acid Copahue fluids that precipitate sulfates such as gypsum and jarosite as well as Fe-oxides may represent a terrestrial analogue to early Mars environments (Parker et al., 2008; Varekamp, 2004). The high P levels in Lake Caviahue derive from the dissolution of volcanic rocks and provide ample nutrients for the local ecosystem. The SO_4 -rich soils of Mars tend to be P-rich as well (Greenwood and Blake, 2006), possibly the result of evaporation of large acid lakes with a composition similar to Copahue hot spring fluids (pH < 1) or to Lake Caviahue waters (pH ~ 2.5). The high P concentrations in the ancient Mars environments should not necessarily be interpreted as the result of a lack of early Martian life at that time (Greenwood and Blake, 2006): the P supply through the dissolution of volcanic rocks in acid fluids may have been larger than the P drawdown by organisms, possibly as a result of N-limitation in the primary producers, as is currently the case in Lake Caviahue.

The Copahue data show similarities with acid fluids from other active arc volcanoes (Varekamp et al., 2000): Mg/Na values in Poás crater lake fluids (~1, Fig. 12) are similar to those in intermediate andesitic rocks; pre-eruptive CP water samples have Mg/Na ~ 0.6, a value identical to mean pre-eruptive Copahue rocks. The post-eruptive CP fluid samples have higher Mg/Na (~1.5), while the

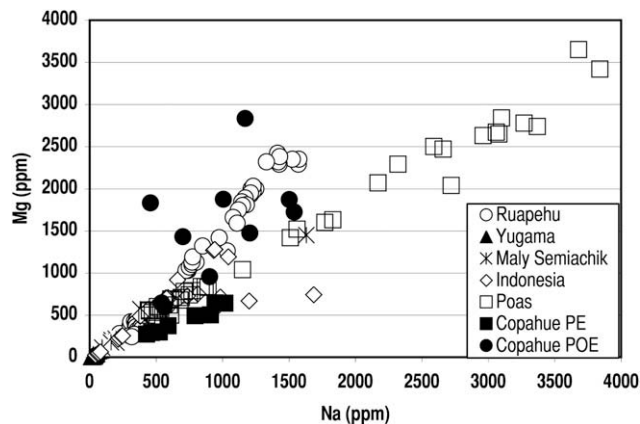


Fig. 12. Na–Mg relations in various hyperacid fluids from active arc volcanoes (data from Varekamp et al., 2000). Slopes of data arrays indicate the dissolution of olivine versus plagioclase and bulk rock dissolution. Note the increased Mg concentrations in Copahue during/after the 2000 eruption (Copahue PE, pre-eruption, and POE, post-eruption, relate to pre-2000 and post-2000 fluids).

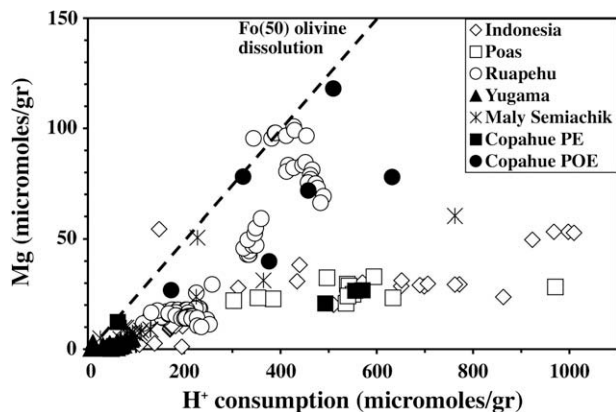


Fig. 13. H^+ consumption diagram for acid volcanic fluids versus Mg concentrations (the H^+ consumption calculations and data from Varekamp et al., 2000). The olivine dissolution line bounds the data to the upper left. All these fluids show the effects of dissolution of multiple minerals and/or glass.

rocks erupted at that time had Mg/Na ~ 0.9. The Mg concentrations in the acid fluids can also be compared with the DON parameter or H^+ consumption (see calculations in Varekamp et al., 2000) that has taken place in the deep fluid during W/R interaction (Fig. 13). The dissolution line of a Mg(50%)-olivine is indicated, and all data points plot below that line, indicating that other H^+ – consuming reactions were ongoing simultaneous with olivine dissolution. The post-eruptive Copahue fluid samples plot closer to the olivine dissolution line, suggesting once more the early dissolution of olivine in the newly intruded magma in 2000. The Na–Al relations in the CP fluids show evidence for plagioclase dissolution (Fig. 14), with the Poás data near the intermediate plagioclase dissolution line (andesine), and most Ruapehu samples near the albite dissolution line. The pre-eruptive Copahue samples plot along the andesine dissolution trend, whereas the post-eruptive samples plot at lower Al concentrations, probably the result of alunite precipitation in the hydrothermal reservoir. The H^+ consumption versus Na concentration diagram shows a broad scatter of data, with the Copahue data plotting with the Ruapehu data towards the labradorite dissolution line (Fig. 15). These diagrams show the commonalities between these acid volcano-hydrothermal systems and the role of preferential dissolution of plagioclase and olivine during the early stages of rock dissolution.

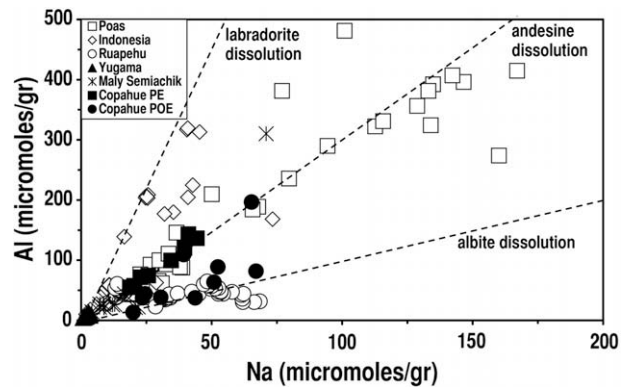


Fig. 14. Diagram of Al versus Na for dissolution of feldspar in acid fluids. Note the decreased Al concentrations in post-eruptive Copahue fluids, suggesting Al depletion through alunite precipitation (data from Varekamp et al., 2000).

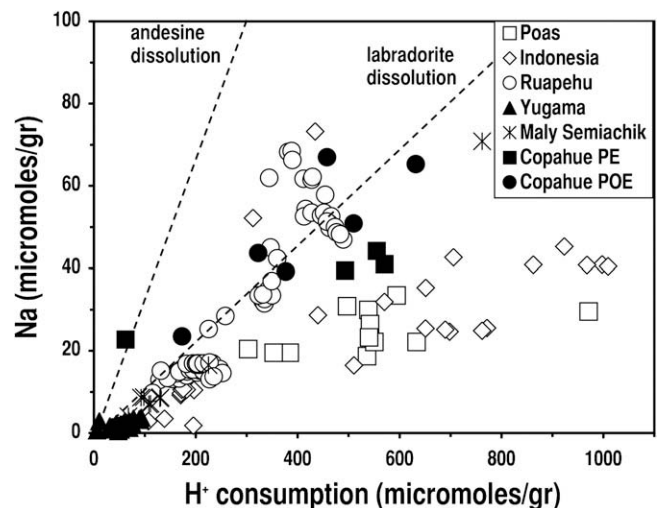


Fig. 15. H^+ consumption diagram for plagioclase dissolution, with the post-eruptive Copahue fluids (POE) showing enhanced rates of feldspar dissolution relative to the pre-eruptive (PE) fluids.

These hot, acid and shallow volcano-hydrothermal fluids may be a crude analog of subduction zone fluids that mobilize elements from the subducted crust and sediment, although the pressure and temperature conditions are of course very different. If this analogy holds, the subduction fluids would not dissolve Nb and Ta, whereas both U and Th would be largely mobilized, contrary to the common view (Bailey and Ragnarsdottir, 1994). The LREE would be enriched in these fluids relative to the rock matrix, and most incompatible trace elements quantitatively extracted. Such element fractionations are commonly invoked to explain the composition of arc volcanic rocks (e.g., Winter, 2001).

7. Conclusions

The time series of the composition and fluxes of the Copahue acid hydrothermal fluids provide several new insights. Many incompatible elements show close to congruent dissolution behavior, whereas the high field strength elements are largely immobile, even in these hot and hyperacid fluids. The elements U and Th show similar, pseudo-congruent dissolution behavior, with little fractionation between the two elements.

During the pre-eruptive period at Copahue, many major element ratios are similar to those in mean bulk rock, suggesting that fine-grained crystallized rock or a glassy matrix was available for W/R interaction. The DON values were around 50% but then decreased towards lower values by late 1999, possibly signaling enhanced volcanic gas inputs from rising magma. The REE patterns during this period showed enrichment in LREE relative to the rock. During the 2000 eruption, the hot spring fluids became more concentrated, the REE pattern became closer to that of the bulk rock, and the fluxes of Mg, Na, Fe and Al increased strongly. In the years following the 2000 eruption, strong variations in element ratios occurred, and the REE became heavily fractionated in both the HREE as well as the LREE. The negative Eu anomaly in the pre-eruptive fluids decreased in magnitude during the 2000 eruption and in late 2004 (Eu/Eu^* increased). In late 2004, the REE pattern became similar to bulk rock values, and possibly, a small intrusion of magma occurred, which did not lead to an eruption however. This new magma provided fresh plagioclase crystals that were rapidly dissolved, leading to the decrease in the magnitude of the negative Eu anomalies in the CP fluids. In 2006, the system had ‘calmed down’ again, and Lake Caviahue had resumed its overall dilution trend (Varekamp, 2008).

The chemical signatures in the source fluids may be used in eruption forecasting: increases in the Mg/Cl and Mg/K values, increase in Eu/Eu^* , and more “rocklike” REE patterns all may point to the incipient dissolution of newly intruded magma into the acid hydrothermal reservoir, possibly foreboding a new eruptive period. Increases in S/Cl may also be related to intrusion of new magma, given the lower solubility of SO_2 relative to HCl in most magmas at shallow depth (e.g., Symonds et al., 1994). Toxic element (As, Li, B) fluxes from Copahue into the local environment are significant, but on a global basis they contribute only a small proportion of the total aqueous toxic element load to the oceans (e.g., Varekamp and Thomas, 1998).

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