Aqueous geochemistry of an active magmato-hydrothermal system: Copahue Volcano, Río Agrio, and Lake Caviahue, Neuquén, Argentina

by

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CHAPTER 1: INTRODUCTION

1.1 Hydrothermal Emissions As Sentinels for Dormant Volcanoes

Many dormant and active volcanoes have fumarolic emissions that may range from quiet CO₂-rich gas vents, to high temperature fumaroles, to boiling mudpots, to active acid crater lakes (Varekamp et al, 2000; 2014). The compositions of fluids and gases vented reflect the ongoing hydrothermal processes below the volcano superstructure at the interface of the magma chamber and the water table and volcanic edifice (Varekamp et al, 2000). Studies of these fluids, both in terms of changes in output of chemicals and heat as well as changing chemical compositions over time, may be used for volcano monitoring, as well as gaining insights into magmato-hydrothermal interactions. In addition, these hydrothermal systems may be tapped for geothermal energy. Many of the active systems may be seen as analogs for ore forming brines of the past that created the massive ore bodies in eroded volcanic structures, such as porphyry copper deposits (Henley, 1985). This study uses the chemistry of fluids collected just after the eruption of an active volcano, and documents the composition and fluxes of current emissions and put these into context with a time series of data at Copahue from 1997 to 2013.

1.2 Copahue Volcano

1.2.1 Geologic Setting

Copahue Volcano is an active 2,997m glaciated stratovolcano that straddles the border of Chile and Argentina’s Neuquén province, at 37.53°S, 71.10°W, in the northeastern side of the Southern Volcanic Zone (SVZ) of the Andes (Varekamp et al, 2001). Copahue is situated in the Caviahue caldera (alternately known as the Agrio caldera), a 3-4 Ma 300km² collapse caldera (Melnick et al, 2006). The Caviahue caldera contains Lake Caviahue, a large glacial lake that has been acidified by hydrothermal fluids.
from Copahue. This section will introduce the stratigraphy and volcanology of Copahue, followed by a description of its surface hydrothermal features.

The volcanology of the Caviahue-Copahue Volcanic Complex (CCVC) has been characterized by Delpino and Bermudez, 1993; González and Vergara, 1962; Linares et al, 1999; Melnick et al. 2006; Muñoz and Stern, 1988; Niemeyer and Muñoz, 1983; Pesce, 1989; Suárez and Emparán, 1997; Varekamp et al, 2006; Vergara and Muñoz, 1982; among others, who categorize Copahue’s evolution through a set of local stratigraphic units. I follow here largely the overview from Melnick et al (2006), who distinguished a set of rock units belonging to the Plio-Pleistocene Caviahue series and a set of formations that form the quaternary Copahue volcano (figure 1.1).

The Cola de Zorro (CdZ) formation is made of andesitic lavas, volcanic breccias, and some sedimentary members, makes up the caldera walls and basement (González and Vergara, 1962; Melnick et al, 2006). The CdZ Fm is well exposed between 36° and 39°S, with K-Ar ages between 5-1 Ma (Vergara and Muñoz, 1982; Niemeyer and Muñoz, 1983; Suárez and Emparán, 1997; Linares et al, 1999). Deposition of CdZ rocks that make up the Caviahue caldera walls and basement is constrained to between 5.6±0.1 Ma and 4.0±0.1 Ma using K-Ar (Muñoz and Stern, 1988). CdZ ranges in thickness between 100m and 1200m and is heavily faulted; structural features indicate the formation was deposited during an extensional faulting regime that continued after the end of deposition (Melnick et al, 2006).

The Las Mellizas (LM) sequence is the first post-caldera unit, and overlies the CdZ with an erosional unconformity representing a 1.5 million-year gap in volcanic activity. LM is made up of lower lavas, ignimbrites, and upper lavas, ranging in age between 2.68±0.14 Ma and 2.60±0.1 Ma (Linares et al, 1999). The LM formation is considered
to be the ancestor of the modern Copahue sequence, with its main emission center located where Copahue is today (Melnick et al, 2006; Pesce, 1989). Coeval with early Copahue volcanics are the Trolope lava flows (TL), is situated in the northeastern corner of the Caviahue caldera. TL date between 1.63±0.1 Ma and 0.82±0.16 Ma and are associated with an isolated feeder dike (Linares et al, 1999; Melnick et al, 2006).

Fig. 1.1 Generalized stratigraphic column of the main lithologies and maximal thicknesses of the Caviahue-Copahue complex (Melnick et al, 2006).
1.2.2 Recent Eruptive History

The Copahue volcano consists of the modern volcanic edifice as well as the surrounding lavas and pyroclastic deposits, with the oldest deposits dated at 1.23±0.18 Ma (Muñoz and Stern, 1988; Linares et al, 1999). The main edifice-building period lasted until 0.76±0.14 Ma, and eruptive and effusive activity has continued in various capacities to the present (Muñoz and Stern, 1988, Melnick et al, 2006). The Plio-Pleistocene units are scarred by glacial abrasion and overlain by till deposits, while younger sequences are absent of glacial erosion. A synglacial dome sequence made up of andesitic and dacitic flows exhibit features consistent with interaction between lava and water, including polygonal fractures, glassy margins with pseudopillow cracks, and well-developed pillow lavas (Melnick et al, 2006).

Explosive deposits made up of massive pyroclastic deposits as well as smaller basaltic-andesitic lavas that are relatively homogeneous in composition dominate post-glaciation volcanics. Postglacial activity continued intermittently during the Holocene; exposed pyroclastic flows have radiocarbon dates ranging between 8770±70 and 2280±50 years BP (Cecioni et al, 2000; Polanco et al, 2000; Melnick et al, 2006). At least 12 major historical eruptions have occurred in the past 300 years, all with a VEI of ~2 (Smithsonian Institution, 2013).

The most recent phase of activity began in July 1992 with a phreatomagmatic eruption; phreatic crater lake explosions of hydrothermally altered rock fragments and liquid sulfur occurred in December 1994 and 1995 (Bermudez and Delpino, 1995; Delpino and Bermudez, 1993). A series of phreatomagmatic and magmatic eruptions began in July 2000 and continued into early 2001, with continuous degassing between eruptive events (Naranjo and Polanco, 2004; Varekamp et al, 2001). In 2004 there was
increased seismic activity, enhanced fluxes from the hot springs (Varekamp et al, 2009) but freezing over of the crater lake (thermal anomaly of Agusto et al., 2013), however no eruption occurred.

On December 22, 2012, there was a magmatic eruption (VEI 2) lasting close to 24 hours, producing an ash plume with pumice fragments, scoria and cinders, and the late stage activity was characterized by fire fountains and strombolian type activity (Camfield et al, 2013). Degassing was nearly continuous through November 2013, with occasional ash explosions. In May of 2013 approximately 3000 people were evacuated from the surrounding region in both Chile and Argentina as the volcanic alert was raised to orange; these concerns were not borne out and the region was repopulated a few weeks later. Alert status remained at yellow from June 2013 to mid-March, 2014, and was raised to orange in late March, 2014 due to heightened seismicity and gas flux (Global Volcanism Program, 2014).

Photo 3 December 22, 2013 eruption seen from the north of Lake Caviahue. © AFP
1.2.3 Copahue Hydrothermal System

The name “Copahue” means “sulfur waters” in the local Mapuche language; its name refers to the acid-sulfate hydrothermal fluids that surface in the summit crater lake and hot springs around its summit. These hydrothermal fluids consist of mixtures of meteoric water (glacial meltwater) and magmatic waters and volcanic gases (Ouimette, 2000; Varekamp et al, 2001). The summit crater lake is a mixture of glacial meltwater, meteoric water, and deep magmato-hydrothermal fluids that rise from the volcanic hydrothermal system into the bottom of the crater lake. The crater lake was blown away during summit eruptions, and later refilled. In March 2013 the crater lake had not yet recovered from the December 2012 eruption, though it may since have refilled following the austral winter. The crater lake contains an acid brine (pH 0.1-0.3), with temperature and color varying widely over the past sixteen years. Temperature has ranged between 0°C (August 2004) to 42°C (June 2005); crater lake water color has ranged from a bright sulfuric green, to milky white, to clear and blue (Agusto et al, 2012; Varekamp et al, 2001; 2009). Dense clouds of HCl gas hover over the surface of the crater lake when it is hot (Varekamp et al, 2001; Varekamp et al, 2009; J.C. Varekamp, personal communication).

Several hot springs emit fluids from Copahue’s hydrothermal system, ranging from highly concentrated acid-sulfate brines (pH<1) to neutral geothermal waters. A geothermal area east of Copahue and north of the town of Caviahue has neutral mineralized hot springs and sulfuric mudpots. The summit hot spring is El Vertedero (CP), the largest and highest in elevation, which produces highly acidified hydrothermal fluids that feed the Upper Río Agrio. The CP hot spring and smaller rivers form the headwaters of the acid Upper Río Agrio, which drains into acidified Lake Caviahue
inside the Caviahue depression, with an outlet through the Lower Río Agrio (Gammons et al, 2005; Geller et al, 2006; Ouimette, 2000; Varekamp et al, 2001; 2003; 2008; 2009).

In addition to the acid crater lake and hot springs, there are a number of hot fumaroles in and near the summit crater that produce HCl, HF, SO₂, CO₂ and other trace volcanogenic gases (Agusto et al, 2013). Northeast of the volcano is a geothermal zone where more neutralized chloride and sulfate hot springs surface, as well as sulfur-rich mud pots (Mas et al, 1996). While the geothermal area is an important tourist destination and local Mapuche village, the hot springs in this area do not appear to have a direct source from Copahue’s magmato-hydrothermal system, but rather result from passive heating flux and alteration by shallow hydrothermal H₂S (Mas et al, 1996).

1.3 The crater lake and summit hot springs

Chemical and isotopic data indicate that the CP hot spring fluids and the crater lake are made up of magmatic fluids with a deep hydrothermal source and glacial meltwater (Ouimette, 2000; Varekamp et al, 2001). These fluids contain high concentrations of
dissolved volcanogenic elements (VE), including fluoride, chloride, and sulfate, as well as high levels of trace metals derived from the high temperature gas emissions that include arsenic, boron, lead, and cadmium (Ouimette, 2000; Varekamp et al, 2001; 2009). The acid hydrothermal fluids in the subsurface Copahue hydrothermal system undergo extensive water/rock (W/R) interaction, leading to high concentrations of dissolved rock forming elements (RFE) in both the crater lake and hot spring fluids.

Consistent differences in chemical and isotopic composition between crater lake fluids and hot spring compositions have been obtained over the years (Ouimette, 2000; Varekamp et al, 2001; 2009), possibly reflecting different sources within the hydrothermal reservoir for these fluids.

The CP fluids tend to be more concentrated in RFE, have different stable isotope compositions and different element ratios, both in RFE and RFE/VE. Most likely, these differences reflect a chemical and physical structure of the underlying system, with the crater lake fed by fluids directly above the core region of the system and the CP springs a more lateral output, possibly with additional W/R interaction in its flow path (Ouimette, 2000, Varekamp et al, 2001; 2009). The variations in composition and elemental flux have been tentatively related to processes inside the hydrothermal reservoir as well the related volcanic activity (Agusto et al, 2012; 2013; Gammons et al, 2005; Geller et al, 2006; Kading, 2010; Ouimette, 2000; Varekamp et al, 2001; 2003; 2008; 2009).

1.4 Río Agrio

The Río Agrio has its headwaters at CP, from whence it flows down the eastern flank of Copahue, joined by several small meltwater tributaries, before it flows into Lake Caviahue’s southwestern shore, south of the town of Caviahue. The northern arm of
Figure 1.3 Map of Neuquén province; zoomed-in section shows the locations of Copahue volcano and Lake Caviahue (top left), as well as the long-term reach of the Lower Río Agrio toward Loncopué, Las Lajas and Zapala (Modified from Instituto Geografico Militar, Argentina, 2013)
Lake Caviahue has an outlet river, the Lower Río Agrio, which leaves the caldera at its northeastern end and then flows for several kilometers through a deep valley before it merges into the Río Norquín and flows further south towards Loncopue (figure 1.3).

### 1.4.1 Upper Río Agrio

The Upper Río Agrio (URA) flows for approximately 14km from close to Copahue’s summit, to the western shore of Lake Caviahue. The URA is strongly acidified and is responsible for the acidification and contamination of Lake Caviahue with VE, RFE and a host of toxic trace elements and nutrients (Agusto et al, 2012; 2013; Gammons et al, 2005; Geller et al, 2006; Kading, 2010; Pedrozo et al, 2008; Ouimette, 2000; Varekamp et al, 2001; 2003; 2008; 2009). Element concentrations in the URA are diluted equivalents of the CP fluids; some of the tributaries are enriched in VE and RFE as well and moderately acidic in some cases (Varekamp et al, 2001). Dilution by these less acidic tributaries and possibly some minor W/R interaction in the riverbed and with suspended sediment raises both the pH of the river water and RFE concentrations, between the summit and its outlet into Lake Caviahue (Varekamp et al, 2001; 2003; 2008; 2009).

The URA’s pH and elemental concentrations fluctuate depending on seasonal variations in flow rate as well as changes in the chemistry of the CP hot spring (Varekamp, 2008; Varekamp et al, 2009). Year-round data on URA flow rates are lacking, but Varekamp (2008) used several years of river flow measurements in conjunction with the hydrology study of Rapacioli (1985) to create an estimated year-round water flux record for the URA. The estimated seasonal water flow range is between 0.4 m$^3$/s in the fall and 3.9 m$^3$/s in the spring, with a mean annual flow rate of 2.6 m$^3$/s, in agreement with field data and model results (figure 1.4). The URA thus has a modeled annual water flux of between 66-83x10$^6$ m$^3$ (Varekamp, 2008).
Figure 1.4 Modeled URA water flow (heavy dashed line – maximum flow of 2.9 m$^3$/s; light dashed line – maximum flow of 3.9 m$^3$/s). URA cross-section data are heavy marked line; LRA flow data are square points (Varekamp, 2008).

Photo 4 URA waterfall near beginning of Copahue’s steep edifice, March 2013.
1.4.2 Lower Río Agrio

Flowing out of the eastern corner of the north arm of Lake Caviahue, the Lower Río Agrio (LRA) flows east and north out of the caldera for 9km before it joins the neutral Río Norquín (RN), which flows east and south into the Loncopue valley. The flow rate of the LRA is dependent on the lake level; observed water flow rates (usually taken in December or March) indicate a mean annual flow of $86-111 \times 10^6$ m$^3$/year (Varekamp, 2008). The LRA’s composition initially matches that of the lake water, but its pH increases and RFE composition changes within the first few kilometers, as the waters become diluted, the pH rises and some precipitates form. Red-orange minerals (ochers) coated the riverbed almost directly after the lake exit in the years 2006-2013. During the years when the lake water pH is lower, the riverbed ochers precipitated only near the
Salto and beyond (2003), while years with a higher lake water pH correlate with these ochre deposits beginning further upstream (2006 and on; Varekamp, personal communication).

Kading (2010) found that this ochre consisted of Schwertmannite, an iron-hydroxysulfate mineral, that precipitates in acid watersheds with pH 2-4 (Bigham et al., 1996), along with goethite (FeOOH) and possibly jarosite (KFe${}^{3+}$$_{3}$(OH)$_{6}$(SO$_{4}$)$_{2}$). In this particular system, this assemblage appears to be stable only between pH of approximately 3-3.5 (Varekamp, 2008). The precipitation of these minerals alters the LRA water composition, as their major components (Fe, Al, SO$_{4}$) decrease rapidly between the lake outlet and downstream sampling sites; trace elements like As, V, and P are preferentially incorporated and adsorbed onto schwertmannite, and are thus removed from the water at a far greater rate than other trace elements (Acero et al., 2006; Kading, 2010). Gammons et al (2005) described precipitates possibly rich in aluminum at the junction of the LRA and Rio Norquin that had incorporated REE from the waters.

1.5 Lake Caviahue

Lake Caviahue (CVL) is an acidic, dimictic oligotrophic lake located in the floor of the Caviahue caldera. It has two 10 km by 4 km arms whose long axes run east-west, and are connected on the western side by a shallow channel. The lake is up to 90m deep and has a total volume of 0.474 km$^{3}$ and a surface area of 9.22 km$^{2}$ (Rapacioli, 1985). The origin of the two deep basins of CVL is unclear: Melnick et al (2006) suggest the lake is formed by a horst (central peninsula) and graben (basins) structure, while González Díaz (2005) finds glacial excavation, associated with structural weakness of the Caviahue graben, as a potential mechanism for the excavation of the two CVL basins.
The lake is thermally stratified during the austral summer (November to March), with the thermocline at approximately 35m depth. The surface waters reach temperatures up to 18°C and hypolimnion waters stay around 8°C; the water temperature decreases rapidly from 0-35m and then remains relatively constant below the thermocline (Varekamp, 2008). In the austral winter (June to September), the lake is probably fully mixed (no empirical data available, however), with water temperatures ranging from 3.5-5.0°C; it rarely freezes over despite air temperatures consistently below freezing and heavy snowfall (Pedrozo et al, 2008; Varekamp, 2008).

In addition to the input from the URA, CVL also receives a freshwater input from the Agua Dulce, a small glacial meltwater river that enters the lake on the northwestern shore near the town of Caviahue. The Agua Dulce is responsible for approximately
38x10^6 m^3 of annual input to CVL; there are additional small meltwater streams that flow directly into the lake around its margins, and the lake receives direct snowmelt and rainwater runoff in the spring (Varekamp, 2008). The total water input into CVL from all these riverine sources is estimated at 103-120x10^6 m^3 (Rapacioli, 1985; Varekamp, 2008). Assuming 1.8 m of annual precipitation (Rapacioli, 1985), the lake receives an additional 16x10^6 m^3/year of precipitation input. Rapacioli (1985) estimated a water residence time for CVL of 2.6 years, which seems to be too short to explain the changes in composition for the known input functions (Varekamp et al., 2001; Varekamp 2003; 2008). Preliminary studies of E/I (evaporation/river input) based on stable isotope values from the URA and CVL, and evaporation modeling (Varekamp et al, 2004; Varekamp, 2014) suggests also a longer water residence time. Thus the sum of water loss from the lake (LRA outflow + evaporative loss) is 97-122x10^6 m^3/year and the lake water level is in steady state on an annual basis, though it experiences seasonal fluctuations of buildup and drawdown (Varekamp, 2008). Varekamp (2003) found that a mean water residence time of 3.5-4 years (42-48 months) based on mean chemical input and output was in agreement with a calculated maximum Mg residence time of 4 years, using data from 1997-2000.

URA input to CVL contaminates the lake with VE and RFE, rendering the lake water acid (pH 2.5-3) with a small population of phytoplankton (Pedrozo et al, 2008). The composition of CVL waters varies in a non-steady-state dynamic as inputs of VE and RFE fluctuate throughout Copahue’s eruptive cycles (Varekamp, 2003), which coupled with the 3.5-4 year residence leads to trailing signals in the lake water composition.

Volcanogenic phosphorous input to the lake results in an annual P load that is 5-25 times higher than total N; the ecosystem in the lake is therefore N-limited. Pedrozo et al
(2008) find that biomass is decimated during eruptive periods, with only 6% of the original pre-eruption biomass remaining in the lake. Beamund et al (2007) indicate that phytoplankton die-off during an eruptive event results from increased RFE concentrations in the lake, as well as decreased light due to higher quantities of volcanic ash suspended in the water column. However, the phytoplankton community was found to recover to previous species percentages as the lake pH increased from ~2.45 to ~2.75 between March, 2001 and March, 2004 (Pedrozo et al, 2008).

Magmatic activity in Copahue has a significant impact on surface fluids. Geochemical trends in surface hydrothermal fluids and the acid Agrio watershed provide insight to hydrothermal processes within the volcano. Hydrothermal contamination impacts waters many kilometers away from Copahue towards the Loncopue valley. (Gammons et al, 2005; Herman, 1998; Kading, 2010; Ouimette, 2000; Varekamp et al, 2008).

1.6 Research Goals

The goals of this study include the presentation of new chemical and water flux data from fieldwork and sampling performed in March of 2013, just after the late 2012 eruption of Copahue volcano. The new data are then integrated with the aqueous geochemical data for the Copahue-Caviahue hydrothermal system and watershed obtained over the past 17 years (since March 1997). The new 2013 data will be compared with the compositional trends in the hydrothermal effluents and river-lake system after the last eruption in 2000. I hope to provide new insight into Copahue’s eruptive cycles and their reflection in chemical water composition and element fluxes. Furthermore, the new data enable further characterization of the geochemical processes in the URA-CVL-LRA system with its precipitation and dissolution of the ochers over time and associated trace element concentrations in the LRA.
CHAPTER 2: METHODS

2.1 Field Methods

Fieldwork was performed in mid-March, 2013, approximately three months after the December 2012 eruption. It was the end of the austral summer; water flow levels were low, as was the lake water level. Locals to the town of Caviahue indicated it had been an unusually dry summer.

2.1.1 Water sampling

2.1.1.1 Lake Waters

Four Lake Caviahue depth profiles were taken over a period of two days aboard an inflatable rowboat; CVLN profiles were taken day one, and CVLS profiles on day two. Sampling occurred at two locations in each arm of the lake; these locations were recorded with a handheld GPS and attempts were made to counteract drifting during sampling, though the first day significant easterly winds caused some drift. The second day conditions were more favorable, with a clear sky and calm, flat lake. Vertical depth profiles were sampled at 5-meter intervals using a Wildco Teflon Kemmerer sampler tied to nylon rope. The rope was marked at 5m intervals to accurately measure depth of origin of the sample. Temperature and pH measurements were taken in the field with a digital thermometer and field pH meter, respectively (pH was again measured in the lab at local ambient temperature (22°C) with a due to temperature-related change in pH.

Samples were filtered either in the field (CVLNA) or in the lab (all others) using 60ml luer-lock syringes and disposable sterile 0.22µm filters, into either 200ml Nalgene narrow-mouth round bottles or 125ml Nalgene square wide-mouth bottles. Trace element samples were filtered directly into ultraclean 125ml Nalgene bottles and further acidified with HNO₃ within 24 hours, in order to prevent precipitation of trace element-
bearing minerals. All bottles were new and unopened at the time of sampling. Temperature-dependent conductivity measurements were additionally taken in the field along the same profiles to a depth of 150 feet (45.7 m) to assess the anion and cation concentration down the depth profile.

2.1.1.2 River Waters

River waters were sampled using 60 ml luer-lock syringes and filtered with 0.2 µm disposable sterile filters, either in the field (URA 1A and 1B, all CVLNAA samples, and all trace element samples), or in the lab (all major element samples for CVLNBB, CVLSAA, CVLSBB, all LRA, all RN, and URA 2, 6, and XS 3) using the same methods, including refrigeration to original field temperatures. Temperature and pH measurements were taken in the field with a digital thermometer and field pH meter, respectively (pH was again measured in the lab at local ambient temperature (22°C)).

2.1.2 River Cross-sections

To gain water flux data for the Upper and Lower Rio Agrio, we did water flow cross-sections at two locations on the URA and one on the LRA. Water depth and stream flow measurements were taken using a Global Water FP-201 Global Flow Probe at one foot intervals along a given cross-section of the river. Measurements were taken using a measuring tape that was anchored to each bank of the river. Stream flow measurements were taken midway between the surface and bottom of the river for the steadiest flow and to avoid clogging the flow meter with sediment. Depth was measured using a centimeter scale that had been inscribed on the flow meter. In some cases at the URA cross sections, the water was very shallow and the flow meter had to rest on the stream bottom in order to be fully submerged. The first URA cross section, near the lake outlet, needed to be split into two cross sections due to a narrow sandbar in the middle of the
stream. Separate water samples, temperature and pH measurements were taken for these cross sections because a small freshwater stream joined the URA just upstream of the cross-sections. The second URA cross section (URA XS3) was taken in one section as there were no issues with depth of the river.

2.1.3 Solid samples

The solidified mineral samples were collected from the ground near the summit or scraped off of rocks at the highest sampling point of the URA (URA 2). Samples were stored in heavy-duty Ziploc bags for transport back to Wesleyan, where they were later stored in clean 125ml square Nalgene bottles. Ocher mud from the LRA was collected at the Salto del Agrio site, and stored in heavy-duty Ziploc bags prior to analysis.

2.2 Lab Analysis

2.2.1 Filtering

Samples that had not been filtered in the field were filtered in the lab between April 1 and April 8, 2013. Samples that were filtered in the lab were cooled to approximately the temperature they were collected at (~10.5°C). Lab-filtered samples were filtered using the same process as in the field: waters were run through 0.22µm sterile filters using 60ml luer-lock syringes, into new 200ml Nalgene bottles. Some samples, especially the farthest upstream URA sample (URA 2), contained large quantities of suspended sediment and required the use of several filters. URA 2 also had a noticeable sulfur smell when it was filtered.

2.2.2 Lab pH measurements

The pH of all samples was re-measured in the lab with a new electrode at room temperature. The pH meter was calibrated using three WWR pH buffer solutions with pH 1, 4, and 7, before any measurements were taken, as well as periodically throughout
measurement. Samples were measured in order of increasing acidity, with more frequent calibration between more acidic samples.

2.2.3 Water sample IC analysis

All water samples were analyzed for sulfate and chloride using a Dionex dx-500 ion chromatograph (IC). Standards were made using a Dionex 5-Anion standard with an original concentration of 20ppm F, 30ppm Cl, 100ppm Br, 100ppm NO$_3^-$, 150ppm PO$_4^{3-}$ and 150ppm SO$_4^{2-}$. Four standards were made with increasing concentrations, ranging between <0.7 to >8ppm F, and <5 to 60ppm SO$_4^{2-}$. Due to the large quantity of samples, standards were remade several times, and default quantities were accordingly updated.

<table>
<thead>
<tr>
<th>Standard</th>
<th>F (ppm)</th>
<th>Cl (ppm)</th>
<th>Br (ppm)</th>
<th>NO$_3$ (ppm)</th>
<th>PO$_4$ (ppm)</th>
<th>SO$_4$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.66</td>
<td>0.99</td>
<td>3.32</td>
<td>3.32</td>
<td>4.97</td>
<td>4.97</td>
</tr>
<tr>
<td>2</td>
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<td>4.07</td>
<td>13.57</td>
<td>13.57</td>
<td>20.35</td>
<td>20.35</td>
</tr>
<tr>
<td>3</td>
<td>5.02</td>
<td>7.53</td>
<td>25.09</td>
<td>25.09</td>
<td>37.64</td>
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<td>8.13</td>
<td>12.19</td>
<td>40.64</td>
<td>40.64</td>
<td>60.96</td>
<td>60.96</td>
</tr>
</tbody>
</table>

*Table 2.1* Example suite of standards used for IC analysis.

The accuracy of IC measurements decreases above ~60ppm of a given anion, and very high concentrations may damage the machine. Samples were gravimetrically diluted using deionized H$_2$O such that expected SO$_4$ concentrations were well under 60ppm. In the case that a diluted sample’s sulfate concentration unexpected exceeded 60ppm, a new dilution was made and re-run in order to gain more accurate measurements. CVL samples were diluted ~10x, while more concentrated samples (URA, CP) were diluted 50-200x. Dilutions were made in new 200ml Nalgene bottles and decanted into 5ml Dionex PolyVials, with filter caps, for analysis. When transferring samples into the vials, they were run through Dionex ion exchange filters with clean 10ml syringes in order to
filter out cations, especially Fe, which if not removed can precipitate in the column and clog the machine.

The eluent fluid used was made by diluting 3.5 M Na₂CO₃ and 1 M NaHCO₃. Sample run time was initially programmed to 23 minutes, and later shortened to 20, then 15. Peak separation was not an issue at shorter run times because samples only contained measurable amounts of chloride and sulfate. (One sample, CVLSBB 55, contained over 300ppm nitrate, which was confirmed with a second run. This is anomalous for the data set and may be due to contamination from the Caviahue water treatment plant; it is not considered to be related to Copahue’s activity).

Due to the necessary dilutions to keep sulfate levels reasonable, fluoride concentrations were too low for accurate measurements on the IC. Between every few samples during each run, a vial of deionized H₂O was run as an unknown to flush out the column and monitor for anomalous peaks. H₂O sample results were uniformly clean and free of statistically significant disturbances. After analysis, the actual sample concentration was calculated by multiplying the IC result by the dilution factor ($V_2 \times [\text{Concentration}]_{IC} / Sample \ V_1 = [\text{Concentration}]_{\text{actual}}$). Analytical error was calculated using the actual standard concentrations for each run, compared to the analytical concentrations of the standards. In general, error was very low (<1%), and the maximum error was 6.027% (Chloride, Run 10), which only amounts to <0.5ppm uncertainty for these few samples. In addition to the programmed standards, for each run several known standards were analyzed. Results for these standards had similarly low error.
2.2.4 Water sample ICP-AES analysis

All water samples from 2013, as well as 15 CP, URA, LRA, and CVL samples from 2011, 11 CVL samples from 2004, LRA and URA samples from 2008, and a well-known 1992 sample from an Indonesian crater lake, were analyzed for major cations using ICP-AES at Smith College, Northampton MA. Five standards were made using VHG labs MISA standard 6 (all cations except Si) and a VHG single-element Si standard in 5% HNO₃ and used for both runs.

<table>
<thead>
<tr>
<th>Standard</th>
<th>ppm</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>Al</th>
<th>Fe</th>
<th>P</th>
<th>Si</th>
</tr>
</thead>
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<td>0</td>
<td></td>
<td>0.102</td>
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<tr>
<td>4</td>
<td></td>
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<td>47.643</td>
<td>47.643</td>
<td>47.643</td>
<td>47.643</td>
<td>47.643</td>
<td>45.483</td>
</tr>
</tbody>
</table>

Table 2.2 Standards used for ICP-AES analysis of all water samples.

Concentrations for the five standards were selected to span, and exceed, the expected range of concentrations for the samples. More concentrated samples, such as URA and CP samples, were gravimetrically diluted with deionized water. There were two sample runs: the first covered all 2013 and 2008 samples; the second was the 2011 and 2004 samples, and re-analyzed several 2013 samples at different dilutions.

2.2.5 Water and Solids – SGS Laboratories ICP-MS

At the time of sampling in the field, additional samples were taken at select sites for trace element analysis. These water samples were filtered into ultraclean 200ml Nalgene bottles with a 0.2µm filter, and acidified with HNO₃, the same day to prevent trace element loss through precipitation or adsorption. Samples of this type were taken at the summit hot spring (CP1), both URA cross sections (URA 3, URA 1A, URA 1B), LRA cross section, Salto del Agrio, and north of the junction with Río Norquín (LRA XS,
LRA SdA, LRA NJ), one Río Norquín sample (RN 18), and at 15m intervals in the CVLSAA column (CVLSAA 0, CVLSAA 15, CVLSAA 30, CVLSAA 45, and CVLSAA 60). These acidified samples were sent to an SGS S.A. laboratory for ICP-MS analysis of trace metals and rare earth elements (REE).

We samples of the ocher precipitate found in the LRA riverbed that were collected in 2007, 2008, and 2009 as well as our own 2013 sample from the Salto del Agrio analyzed at SGS laboratories. Samples were acid-digested and analyzed by ICP-MS. The muddy precipitate analyzed was found dried on rocks as well as under the water; when still wet it had a slimy algae-like texture. Prior to shipment to SGS, samples were dried in a warm oven and pulverized. A sample taken from the top of a CVL sediment core taken in 2004 (core depth = 0cm) was analyzed as well by the same method.

2.3 Geochemical Modeling

2.3.1 WebPHREEQ

Data from CP and CVL fluids collected from 1997-2013 were used in WebPHREEQ, a simplified, open-source web-based aqueous geochemical modeling tool developed by B. Saini-Eidukat, based on the desktop modeling tool PHREEQC developed by D. Parkhurst (1998). WebPHREEQ uses major and minor element data, along with environmental conditions (temperature, pH, redox conditions, pO$_2$ and pCO$_2$). “Simple speciation” may be calculated using a single set of environmental conditions. “Advanced speciation” adds the option of up to four equilibrium phases (with desired saturation indices) as well as a reaction temperature series in a specified number of steps. Both speciation models may include a single solution or a mixture of two solutions. The WebPHREEQ model reads the input data, checks charge balance and corrects K values for temperature and pressure if necessary. It then uses the
Newton-Raphson technique to iteratively solve non-linear speciation equations simultaneously. The output gives molality and activity for all possible species, as well as saturation indices for any possible mineral phases.

Saturation index (SI) of a mineral indicates whether that mineral is undersaturated, supersaturated, or at equilibrium in the solution at given environmental conditions. The log of the ion activation product (IAP) and the solubility product ($K_s$) of a mineral gives the SI of that mineral. At equilibrium, when IAP = $K_s$, SI = 0. If IAP < $K_s$, the mineral is undersaturated (SI < 0); a supersaturated mineral (IAP > $K_s$) has SI > 0.

2.3.2 Excel

WebPHREEQ provides saturation calculations for a limited number of minerals; schwertmannite is a relatively uncommon mineral with varying stoichiometry and is not included in WebPHREEQ. However, the ion activity coefficients calculated in WebPHREEQ can be used to individually calculate the saturation index of schwertmannite. Kading (2010) developed an excel model for schwertmannite saturation in CVL fluids, using speciation model results from Geochemist’s Workbench. Kading used the average stoichiometry of schwertmannite – $\text{Fe}_8\text{O}_4(\text{OH})_{5.24}(\text{SO}_4)_{1.38}$ – and the Bigham et al (1986) solubility constant for this mineral. The same approach was used in Excel for this study’s calculations for schwertmannite.
<table>
<thead>
<tr>
<th>Phase</th>
<th>SI</th>
<th>log IAP</th>
<th>log KT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)₃(a)</td>
<td>-2.57</td>
<td>0.32</td>
<td>2.89</td>
</tr>
<tr>
<td>Albite</td>
<td>-10.15</td>
<td>-9.64</td>
<td>0.51</td>
</tr>
<tr>
<td>Ałuinite</td>
<td>1.21</td>
<td>-15.19</td>
<td>-16.41</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>0.79</td>
<td>-7.60</td>
<td>-8.38</td>
</tr>
<tr>
<td>Anorthite</td>
<td>-10.93</td>
<td>-5.63</td>
<td>5.31</td>
</tr>
<tr>
<td>Ca-Montmorillonite</td>
<td>-7.79</td>
<td>-10.27</td>
<td>-2.48</td>
</tr>
<tr>
<td>Chaledony</td>
<td>-0.85</td>
<td>-2.99</td>
<td>-2.14</td>
</tr>
<tr>
<td>Chlorite(14A)</td>
<td>-33.92</td>
<td>-10.78</td>
<td>23.14</td>
</tr>
<tr>
<td>Chrysothile</td>
<td>-24.28</td>
<td>-7.45</td>
<td>16.83</td>
</tr>
<tr>
<td>Fe(OH)₃(a)</td>
<td>-13.51</td>
<td>1.51</td>
<td>15.02</td>
</tr>
<tr>
<td>FeS(ppt)</td>
<td>-6.07</td>
<td>-25.67</td>
<td>-19.60</td>
</tr>
<tr>
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<td>4.80</td>
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<td>-5.87</td>
</tr>
<tr>
<td>H₂(g)</td>
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<td>-4.42</td>
<td>-0.00</td>
</tr>
<tr>
<td>H₂O(g)</td>
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<td>-0.00</td>
<td>-1.63</td>
</tr>
<tr>
<td>H₂S(g)</td>
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<td>-25.40</td>
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<tr>
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<tr>
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<td>0.86</td>
</tr>
<tr>
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<td>11.04</td>
</tr>
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<td>-0.59</td>
</tr>
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<td>-9.54</td>
<td>-5.93</td>
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<td>-2.23</td>
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<td>-3.11</td>
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<td>Mackinawite</td>
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<td>-20.34</td>
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<td>-8.01</td>
<td>-1.49</td>
</tr>
<tr>
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<td>42.32</td>
</tr>
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<td>-46.48</td>
</tr>
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<td>-2.99</td>
<td>-2.19</td>
</tr>
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<td>12.56</td>
</tr>
<tr>
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<td>Talc</td>
<td>-20.97</td>
<td>-13.42</td>
<td>7.56</td>
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---

**End of simulation.**

---

**Table 2.3** Excerpt WebPHREEQC output, showing mineral saturation indices. Shown are the results for CP 2013, run at 230°C, pe = 1. Not shown: solution composition, description of solution, and distribution of species.
CHAPTER 3: RESULTS

3.1 El Vertedero Hot Spring

3.1.1 Major Elements

The composition of the CP hot spring was analyzed for the 2013 sample, as well as an as-yet-unanalyzed sample collected by Kading in 2011. The pH value was very similar for both years at 1.1-1.2, the temperature in 2013 was 25°C; temperature was not available for the 2011 sample. The VE concentrations were different between the two samples, with Cl 10 times more diluted in 2013 relative to 2011 (Cl 2013=363 ppm). The sulfate levels decreased by a factor of 3 over that same time, from over 20,000 ppm $\text{SO}_4$ in 2011 to 7600 ppm $\text{SO}_4$ in 2013. The RFE had high concentrations in both samples of several 100 to $>2000$ ppm of the major elements (Table 3.1). Between 2011 and 2013, the Al, Fe, Na and K dropped roughly by a factor of three whereas the Mg concentration decreased by a factor $\sim 2$. The analytical data in Table 3.1 show this complex pattern of increases and decreases of the major elements between the two sample dates.

<table>
<thead>
<tr>
<th></th>
<th>CP 2011</th>
<th>CP 2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
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<td>1.2</td>
</tr>
<tr>
<td>F</td>
<td>ND</td>
<td>14</td>
</tr>
<tr>
<td>Cl</td>
<td>5135</td>
<td>363</td>
</tr>
<tr>
<td>$\text{SO}_4$</td>
<td>20013</td>
<td>7599</td>
</tr>
<tr>
<td>Al</td>
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<tr>
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<td>863</td>
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<td>129</td>
</tr>
<tr>
<td>Si</td>
<td>100</td>
<td>58</td>
</tr>
</tbody>
</table>

Table 3.1 Major elements in 2011 and 2013 samples of CP waters (ppm). ND – not detected at necessary dilution levels.
3.1.2 Trace Elements

CP 2013 is enriched in As (1370 ppb), V (981 ppb), Sr (6210 ppb), and other trace metals (See appendix A for full table). CP water from March 2013 shows overall REE enrichment relative to chondrite, especially among the LREE. CP water is positively enriched in all REE, with the highest enrichment factors among the LREE. The most significant positive excursions are of Sm, Tb, Ho, Tm, and Lu (see Appendix A.1 for full 2013 REE results).

La/Sm gives an average magnitude of LREE enrichment, as congruent dissolution would yield a ratio of ~1. 2012 Copahue rock is moderately enriched in LREE, with La/Sm of 4.7 (absolute values) and 2.96 (rock/chondrite values). In contrast, the absolute La/Sm of 2013 CP fluids is 6.16; the ratio of the CP values normalized to Copahue rock \(\frac{(La_{\text{CP}}/La_{\text{Copahue}})/(Sm_{\text{CP}}/Sm_{\text{Copahue}})}\) is 1.311. Even when normalized to Copahue rock values, the fluids still show significant REE enrichment. Copahue rock-normalized values of 2013 CP fluids show a slightly more negative Eu depletion relative to values from previous years. CP fluids are more strongly depleted in Eu and Gd than corresponding Copahue rock values, while the LREE are more strongly enriched in the fluids than in the rock. Neither 2013 CP fluids nor 2012 rock show significant depletion or enrichment of HREE.

3.2 Upper Río Agrio

3.2.1 River Cross-Sections

The first cross section was located just upstream of the URA’s delta into Lake Caviahue, shortly after the confluence of the URA with an unnamed freshwater tributary. Due to a small sandbar in the center of the channel, the cross section was split into two sections: 1A and 1B. The water fluxes for 1A and 1B were 0.274 m³/s and 0.083 m³/s.
respectively, for total water flow rate of 0.358 m$^3$/s for the river here. 1A and 1B were treated as different sampling sites, as the freshwater tributary was not fully mixed before the river divided. URA 1A concentrations were slightly lower than 1B, and pH was slightly higher, resulting from freshwater dilution.

The third cross section was taken upstream of the town of Caviahue, just downstream of where the URA narrows in a small canyon near some small Mapuche edifices. Total flow rate at this cross section is 0.336 m$^3$/s.

**Figure 3.1** URA 1A cross section flow rate (red) and depth profile (blue). The y-axis values apply to both the flow rate and the depth; units are in m for depth and m$^3$/s for flow rate. Total flow rate is 0.274 m$^3$/s.
Figure 3.2 URA 1B cross section flow rate (red) and depth profile (blue). Total flow rate is 0.083 m$^3$/s.

Figure 3.3 URA 3 cross section flow rate (red) and depth profile (blue). Total flow rate is 0.083 m$^3$/s.
3.2.2 Major Elements

SO$_4$ decreases from 3810 ppm at URA 2, the farthest upstream sample location, to 1237 ppm at URA 1, and 1128 ppm at cross-section 3 (URA XS 3). From URA 2 to URA XS 3 Cl goes from 384 ppm to 348 ppm, though it is much higher at URA 1, an intermediate sampling point, where it is 2258 ppm. At the first cross section site (samples URA 1A and URA 1B) the bulk composition, calculated from the proportion of water volume flux at the two parts of the cross sections, is 137 ppm Cl and 903 ppm SO$_4$. Bulk RFE for that cross section are 74 ppm Al, 46 ppm Fe, 89 ppm Mg, 104 ppm Ca, 53 ppm Na, 21 ppm K, and 31 ppm Si.

<table>
<thead>
<tr>
<th>Sample</th>
<th>URA 1A</th>
<th>URA 1B</th>
<th>URA 3</th>
<th>URA 1</th>
<th>URA 2</th>
<th>URA 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>T °C</td>
<td>10.6</td>
<td>10.4</td>
<td>10.0</td>
<td>11.7</td>
<td>14.5</td>
<td>9.7</td>
</tr>
<tr>
<td>pH</td>
<td>2.6</td>
<td>2.5</td>
<td>2.46</td>
<td>2.5</td>
<td>1.6</td>
<td>6.1</td>
</tr>
<tr>
<td>Cl (ppm)</td>
<td>923</td>
<td>284</td>
<td>348</td>
<td>2258</td>
<td>384</td>
<td>1227</td>
</tr>
<tr>
<td>SO4 (ppm)</td>
<td>839</td>
<td>1114</td>
<td>1128</td>
<td>1237</td>
<td>3811</td>
<td>258</td>
</tr>
<tr>
<td>Al (ppm)</td>
<td>69</td>
<td>901</td>
<td>89</td>
<td>91</td>
<td>398</td>
<td>1.4</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>43</td>
<td>57</td>
<td>55</td>
<td>54</td>
<td>242</td>
<td>0</td>
</tr>
<tr>
<td>Mg (ppm)</td>
<td>85</td>
<td>105</td>
<td>106</td>
<td>106</td>
<td>203</td>
<td>43</td>
</tr>
<tr>
<td>Ca (ppm)</td>
<td>99</td>
<td>122</td>
<td>123</td>
<td>124</td>
<td>267</td>
<td>49</td>
</tr>
<tr>
<td>Na (ppm)</td>
<td>51</td>
<td>61</td>
<td>62</td>
<td>62</td>
<td>162</td>
<td>20</td>
</tr>
<tr>
<td>K (ppm)</td>
<td>20</td>
<td>24</td>
<td>24</td>
<td>24</td>
<td>80</td>
<td>6.4</td>
</tr>
<tr>
<td>Si (ppm)</td>
<td>30</td>
<td>34</td>
<td>33</td>
<td>32</td>
<td>51</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 3.2 URA major elements – 2013 samples.

Along the reach of the URA, S/Cl decreases from the headwaters (CP) to the lake delta – from 7.732 to 2.763. S/Cl was lowest at the second cross-section site, where it was 1.196. RFE/Cl show similar trends, with the lowest values found at the second cross-section. Cl-normalized values increase slightly at the lake exit due to a sharp decline in Cl, not an increase in concentration of RFE. URA 6, the unnamed tributary sampled near URA 1, has very high Cl (1227 ppm) relative to
Table 3.3 URA S/Cl and RFE/Cl values. Samples are ordered by proximity to CVL: 1A and 1B are closest to the lake delta, URA 2 is farthest upstream. URA 6 is a tributary near the URA 1 sampling site.

<table>
<thead>
<tr>
<th></th>
<th>S/Cl</th>
<th>Mg/Cl</th>
<th>Al/Cl</th>
<th>K/Cl</th>
<th>Na/Cl</th>
<th>Si/Cl</th>
<th>Fe/Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>URA 1A</td>
<td>3.334</td>
<td>1.331</td>
<td>0.983</td>
<td>0.190</td>
<td>0.846</td>
<td>0.412</td>
<td>0.294</td>
</tr>
<tr>
<td>URA 1B</td>
<td>1.446</td>
<td>0.537</td>
<td>0.418</td>
<td>0.076</td>
<td>0.329</td>
<td>0.152</td>
<td>0.127</td>
</tr>
<tr>
<td>URA 3</td>
<td>1.196</td>
<td>0.445</td>
<td>0.337</td>
<td>0.062</td>
<td>0.274</td>
<td>0.119</td>
<td>0.101</td>
</tr>
<tr>
<td>URA 1</td>
<td>0.202</td>
<td>0.069</td>
<td>0.053</td>
<td>0.010</td>
<td>0.043</td>
<td>0.018</td>
<td>0.015</td>
</tr>
<tr>
<td>URA 2</td>
<td>3.658</td>
<td>0.770</td>
<td>1.361</td>
<td>0.188</td>
<td>0.651</td>
<td>0.166</td>
<td>0.399</td>
</tr>
<tr>
<td>URA 6</td>
<td>0.078</td>
<td>0.051</td>
<td>0.002</td>
<td>0.005</td>
<td>0.025</td>
<td>0.021</td>
<td>0.000</td>
</tr>
</tbody>
</table>

3.2.3 Trace Elements

Trace element compositions were analyzed for URA 1A, URA 1B, and URA XS 3.

Table 3.4 shows REE concentrations (ppb) for these three samples. These three samples have near-identical REE assemblages, with most elements varying by <0.5 ppb.

<table>
<thead>
<tr>
<th>(ppb)</th>
<th>URA 1A</th>
<th>URA 1B</th>
<th>URA XS3</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>37.8</td>
<td>38.3</td>
<td>36.4</td>
</tr>
<tr>
<td>Ce</td>
<td>95</td>
<td>96.1</td>
<td>93.3</td>
</tr>
<tr>
<td>Pr</td>
<td>13.6</td>
<td>14</td>
<td>13.5</td>
</tr>
<tr>
<td>Nd</td>
<td>57.6</td>
<td>59.7</td>
<td>57.5</td>
</tr>
<tr>
<td>Sm</td>
<td>12.1</td>
<td>12.5</td>
<td>12.1</td>
</tr>
<tr>
<td>Eu</td>
<td>1.87</td>
<td>1.87</td>
<td>1.81</td>
</tr>
<tr>
<td>Gd</td>
<td>9.5</td>
<td>9.59</td>
<td>9.55</td>
</tr>
<tr>
<td>Tb</td>
<td>1.51</td>
<td>1.52</td>
<td>1.5</td>
</tr>
<tr>
<td>Dy</td>
<td>8.08</td>
<td>8.11</td>
<td>8.2</td>
</tr>
<tr>
<td>Ho</td>
<td>1.65</td>
<td>1.67</td>
<td>1.67</td>
</tr>
<tr>
<td>Er</td>
<td>4.69</td>
<td>4.71</td>
<td>4.77</td>
</tr>
<tr>
<td>Tm</td>
<td>0.637</td>
<td>0.642</td>
<td>0.657</td>
</tr>
<tr>
<td>Yb</td>
<td>4.16</td>
<td>4.16</td>
<td>4.24</td>
</tr>
<tr>
<td>Lu</td>
<td>0.648</td>
<td>0.643</td>
<td>0.661</td>
</tr>
<tr>
<td>Y</td>
<td>59.2</td>
<td>61.3</td>
<td>61.5</td>
</tr>
</tbody>
</table>

Table 3.4 Rare earth element (REE) data for the URA cross-section sites (ppb).

These three URA samples were also analyzed for a suite of trace elements; see Appendix A.2 for full results. Trace element concentrations were generally similar among the three URA samples; differences in concentration did not change more than a
few percent for most elements. All samples had high levels of As (~90 ppb), P (760-820 ppb), V (~135), and Pb (~32 ppb), among others.

3.2.4 Element export fluxes

Total monthly element export is calculated using the averaged concentration values from URA 1A and URA 1B in conjunction with the water flux data. Total VE export (Cl + SO₄) is 978 tonnes/month, and total RFE export is 394 tonnes/month (table 3.3). Export of selected trace elements is shown in table 3.3 as well; total export of all trace elements analyzed in URA 1A and URA 1B is 2280 kg/month.

<table>
<thead>
<tr>
<th>Major elements</th>
<th>tonnes/month</th>
<th>Trace elements</th>
<th>kg/month</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>129.1</td>
<td>As</td>
<td>85.1</td>
</tr>
<tr>
<td>SO₄</td>
<td>848.5</td>
<td>P</td>
<td>714.4</td>
</tr>
<tr>
<td>Al</td>
<td>69.9</td>
<td>Cu</td>
<td>20.9</td>
</tr>
<tr>
<td>Fe</td>
<td>43.5</td>
<td>Zn</td>
<td>138.8</td>
</tr>
<tr>
<td>Mg</td>
<td>84.0</td>
<td>U</td>
<td>1.7</td>
</tr>
<tr>
<td>Ca</td>
<td>98.1</td>
<td>V</td>
<td>129.0</td>
</tr>
<tr>
<td>Na</td>
<td>50.0</td>
<td>Ti</td>
<td>148.5</td>
</tr>
<tr>
<td>K</td>
<td>19.3</td>
<td>Sr</td>
<td>639.0</td>
</tr>
<tr>
<td>Si</td>
<td>29.3</td>
<td>Pb</td>
<td>30.1</td>
</tr>
</tbody>
</table>

Table 3.5 2013 URA element export of major VE and RFE as well as selected trace elements, calculated from analytical element concentrations and water flux measurements from March 2013.

3.3 Lake Caviahue

3.3.1 Major Elements

<table>
<thead>
<tr>
<th></th>
<th>T (ºC)</th>
<th>pH</th>
<th>Cl</th>
<th>SO₄</th>
<th>Al</th>
<th>Fe</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVLNA</td>
<td>10.6</td>
<td>2.80</td>
<td>93.3</td>
<td>341.5</td>
<td>29.5</td>
<td>19.0</td>
<td>19.2</td>
<td>25.0</td>
<td>15.5</td>
<td>6.4</td>
<td>14.2</td>
</tr>
<tr>
<td>CVLN1B</td>
<td>10.4</td>
<td>2.72</td>
<td>94.7</td>
<td>338.8</td>
<td>28.6</td>
<td>20.3</td>
<td>20.1</td>
<td>26.4</td>
<td>16.0</td>
<td>6.5</td>
<td>14.8</td>
</tr>
<tr>
<td>CVLSA</td>
<td>10.1</td>
<td>2.83</td>
<td>91.1</td>
<td>331.1</td>
<td>27.8</td>
<td>20.0</td>
<td>19.6</td>
<td>25.5</td>
<td>15.6</td>
<td>6.3</td>
<td>14.8</td>
</tr>
<tr>
<td>CVLSB</td>
<td>10.7</td>
<td>2.75</td>
<td>90.5</td>
<td>328.3</td>
<td>27.9</td>
<td>20.0</td>
<td>19.7</td>
<td>25.7</td>
<td>15.8</td>
<td>6.3</td>
<td>14.8</td>
</tr>
<tr>
<td>Average</td>
<td>10.5</td>
<td>2.8</td>
<td>92.4</td>
<td>334.9</td>
<td>28.5</td>
<td>19.8</td>
<td>19.7</td>
<td>25.6</td>
<td>15.7</td>
<td>6.4</td>
<td>14.6</td>
</tr>
</tbody>
</table>

Table 3.6 Average major element concentrations for 2013 CVL depth profiles and the bulk lake. Each depth profile was measured from 0 to 60 m depth, with a sample taken every 5 m.
Table 3.7 March 2011 CVL data from 2011 depth profile, with averages for all VE and major RFE. Sample name gives depth (m) at the end. This profile was taken in the northern arm of the lake. Temperature data unavailable.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Cl</th>
<th>SO4</th>
<th>Al</th>
<th>Fe</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
<th>Si</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVL-N0</td>
<td>2.76</td>
<td>89.5</td>
<td>336.5</td>
<td>27.4</td>
<td>21.1</td>
<td>20.8</td>
<td>25.7</td>
<td>16.0</td>
<td>6.0</td>
<td>14.9</td>
<td>0.33</td>
</tr>
<tr>
<td>CVL-N10</td>
<td>2.83</td>
<td>90.2</td>
<td>337.6</td>
<td>28.3</td>
<td>21.6</td>
<td>21.4</td>
<td>26.5</td>
<td>16.7</td>
<td>6.3</td>
<td>15.1</td>
<td>0.34</td>
</tr>
<tr>
<td>CVL-N20</td>
<td>2.8</td>
<td>89.3</td>
<td>329.8</td>
<td>28.8</td>
<td>21.7</td>
<td>21.7</td>
<td>25.9</td>
<td>16.9</td>
<td>6.2</td>
<td>14.9</td>
<td>0.35</td>
</tr>
<tr>
<td>CVL-N30</td>
<td>2.9</td>
<td>101.3</td>
<td>369.1</td>
<td>30.1</td>
<td>23.2</td>
<td>22.8</td>
<td>28.1</td>
<td>17.9</td>
<td>6.6</td>
<td>16.1</td>
<td>0.36</td>
</tr>
<tr>
<td>CVL-N40</td>
<td>2.9</td>
<td>91.3</td>
<td>346.5</td>
<td>27.9</td>
<td>21.7</td>
<td>21.1</td>
<td>25.8</td>
<td>16.4</td>
<td>6.1</td>
<td>14.9</td>
<td>0.36</td>
</tr>
<tr>
<td>CVL-N50</td>
<td>2.94</td>
<td>92.3</td>
<td>351.7</td>
<td>28.3</td>
<td>22.1</td>
<td>21.4</td>
<td>26.3</td>
<td>16.6</td>
<td>6.2</td>
<td>15.1</td>
<td>0.34</td>
</tr>
<tr>
<td>CVL-N60</td>
<td>2.94</td>
<td>96.3</td>
<td>354.8</td>
<td>28.9</td>
<td>22.7</td>
<td>21.9</td>
<td>26.7</td>
<td>17.1</td>
<td>6.3</td>
<td>15.4</td>
<td>0.36</td>
</tr>
<tr>
<td>Average</td>
<td>2.87</td>
<td>92.9</td>
<td>346.6</td>
<td>28.5</td>
<td>22.0</td>
<td>21.6</td>
<td>26.4</td>
<td>16.8</td>
<td>6.3</td>
<td>15.2</td>
<td>0.3</td>
</tr>
</tbody>
</table>

**Figure 3.4** Lab pH of CVL depth profiles measured in March 2013.

The 2013 CVL samples showed generally similar compositions, with some variation with depth and location throughout the lake. 2011 and 2013 values were similar, with similar pH as well as VE and RFE concentrations. Average pH in 2013 was 2.8; pH by depth varied among the profiles (figure 3.4); the western profiles (CVLN, CVLS) had...
lower pH values at the surface, with a gradual increase in pH with depth; the eastern profiles (CVLNA, CVLSA) had more homogenous pH throughout the depth profile. The profile sampled in 2011 (table 3.7) had an average pH of 2.87, with lowest pH at the surface and highest pH at depth. Temperature data were not available from the 2011 profile. 2013 profiles had highest temperatures at the surface (11°C-12°C), with a gradual thermocline at around 35 m depth. Water temperatures below the thermocline were ~8°C for all profiles.

In 2013, Na and Mg concentrations decrease slightly with depth across all profiles. CVLNB and CVLSB, the two profiles closest to the URA outlet, are on average slightly more concentrated than the easternmost profiles, CVLNA and CVLSA. In CVLSB and CVLNB, Na and Mg show a slight negative excursion at around 30m followed by a positive excursion around 45m. This increased concentration at 45m depth is also true for Fe and Ca. For most of the cations, the CVLSA and CVLSB profiles tend to be fairly similar to each other, while CVLNA and CVLNB are typically more disparate, or even at one extreme or another. CVLNA has consistently lower Mg, Na, Si, and Fe concentrations than the other three profiles, while CVLNB has the highest concentrations. The only cation that deviates from this norm is Al, whose average concentration in CVLNA (29.55 ppm) is higher than CVLNB, CVLSA, and CVLSB (28.62, 27.84, and 27.86, respectively). The southern arm of the lake remained generally depleted in Al relative to the northern arm. See Appendix B for all depth profile figures.

The URA outlet flows primarily into the northern arm of the lake, and with no other outlets in the southern arm, its waters remain relatively less disturbed by influxes of rock-forming elements (RFE) and volcanogenic anions (VE). Strong easterly winds that occur daily in the region also discourage eastward flow of water from the river outlet to
the southern arm. Based on these physical processes as well as chemical trends in the
four depth profiles, CVLSAA and CVLSBB can be assumed to be older, more well-
mixed water, while CVLNBB (closest to URA outlet) and CVLNAA (closest to LRA
outflow) are subject to more dynamic fluctuations in composition.

3.3.1 Trace Elements

Concentrations of trace metals and REE were measured from 15m intervals in the
CVLSAA profile: 0m, 15m, 30m, 45m, and 60m depth. All trace and rare earth element
assemblages in these samples may not perfectly reflect the other profiles, as can be
expected based on the variations in major element concentrations throughout the lake.

See Appendix A.1 for full REE assemblage. CVLS contained significant concentrations
of As (average 37.4 ppb) and V (average 42 ppb), as well as heightened Pb (average 9.5
ppb) as well as detectable levels of many other trace metals (see Appendix A.2).

Concentrations of As and V were slightly lower in the 0m sample than the other four;
this trend is not reflected among other trace metals.

3.4 Lower Río Agrio

3.4.1 Major Elements

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C)</th>
<th>pH</th>
<th>Cl</th>
<th>SO4</th>
<th>Al</th>
<th>Fe</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>LRA 3 lake outlet</td>
<td>15.9</td>
<td>2.92</td>
<td>91.3</td>
<td>333.8</td>
<td>28.1</td>
<td>19.7</td>
<td>20.0</td>
<td>26.0</td>
<td>15.9</td>
<td>6.4</td>
<td>14.9</td>
</tr>
<tr>
<td>LRA XS (bridge)</td>
<td>9.7</td>
<td>3.1</td>
<td>68.5</td>
<td>255.8</td>
<td>20.2</td>
<td>13.7</td>
<td>15.3</td>
<td>21.0</td>
<td>13.3</td>
<td>5.3</td>
<td>14.6</td>
</tr>
<tr>
<td>LRA SdA</td>
<td>10.8</td>
<td>3.51</td>
<td>70.5</td>
<td>147.4</td>
<td>11.5</td>
<td>0.1</td>
<td>11.2</td>
<td>16.3</td>
<td>9.7</td>
<td>3.8</td>
<td>12.8</td>
</tr>
<tr>
<td>LRA 6</td>
<td>nm</td>
<td>6.4</td>
<td>29.8</td>
<td>103.5</td>
<td>nd</td>
<td>nd</td>
<td>13.8</td>
<td>28.0</td>
<td>9.5</td>
<td>4.7</td>
<td>20.6</td>
</tr>
<tr>
<td>RN 17</td>
<td>nm</td>
<td>6.4</td>
<td>11.8</td>
<td>36.2</td>
<td>1.9</td>
<td>0.3</td>
<td>12.7</td>
<td>30.7</td>
<td>13.9</td>
<td>3.0</td>
<td>19.0</td>
</tr>
<tr>
<td>RN 18</td>
<td>nm</td>
<td>6.5</td>
<td>24.6</td>
<td>99.5</td>
<td>1.7</td>
<td>0.2</td>
<td>13.1</td>
<td>28.0</td>
<td>10.3</td>
<td>4.3</td>
<td>19.7</td>
</tr>
</tbody>
</table>

Table 3.8 Major elements of LRA and Río Norquín (RN) samples collected in 2013. nd – not detected. nm – not measured.

The LRA flows directly out of CVL; the sample taken at the river mouth (sample
code LRA 3) shows similar pH (2.92) and concentrations of VE and RFE to that of the
lake samples (table 3.6; table 3.8). Down the reach of the river, the pH of the water increased; at the cross-section site (sample code LRA XS), pH was 3.1; the Salto del Agrio (sample code LRA SdA) pH had risen to 3.5. Samples were taken of the Río Norquín (RN) before its junction with the LRA (sample code RN 17), and after the LRA joined and appeared to be fully mixed (RN 18). Prior to the influx of the LRA, the RN already had some Cl and SO$_4$ (11.8 and 36.2 ppm, respectively) as well as RFE (30.7 ppm Ca, 12.7 ppm Mg, et al). Like the LRA 6 sample, RN 17 had almost no Al and Fe. RN 18 had 24.6 ppm Cl and 99.5 ppm SO$_4$.

3.4.2 Trace Elements

LRA XS, LRA SdA and RN 18 were analysed for REE and trace elements. LRA XS had 15.9 ppb As, 30 pb Zn, 27.2 ppb V, and 6.63 ppb Pb; LRA SdA had 4.2 ppb As, 0 ppb Zn, 7.92 ppb V, and 4.05 ppb Pb. RN 18 had 0.9 ppb As, 4.58 ppb V, and 0.73 ppb Pb; these samples also had detectable amounts of a number of other trace metals (See Appendix A.2 for full trace element assemblage).

<table>
<thead>
<tr>
<th>(ppb)</th>
<th>LRA XS</th>
<th>LRA SdA</th>
<th>LRA 6</th>
<th>RN 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>6.94</td>
<td>8.01</td>
<td>0.92</td>
<td>0.63</td>
</tr>
<tr>
<td>Ce</td>
<td>15.6</td>
<td>11.4</td>
<td>1.31</td>
<td>0.91</td>
</tr>
<tr>
<td>Pr</td>
<td>2.14</td>
<td>2.05</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>Nd</td>
<td>8.92</td>
<td>8.13</td>
<td>0.81</td>
<td>0.58</td>
</tr>
<tr>
<td>Sm</td>
<td>1.86</td>
<td>1.58</td>
<td>0.15</td>
<td>0.11</td>
</tr>
<tr>
<td>Eu</td>
<td>0.332</td>
<td>0.241</td>
<td>0.022</td>
<td>0.016</td>
</tr>
<tr>
<td>Gd</td>
<td>1.5</td>
<td>1.42</td>
<td>0.14</td>
<td>0.1</td>
</tr>
<tr>
<td>Tb</td>
<td>0.23</td>
<td>0.215</td>
<td>0.014</td>
<td>0.003</td>
</tr>
<tr>
<td>Dy</td>
<td>1.28</td>
<td>1.21</td>
<td>0.119</td>
<td>0.087</td>
</tr>
<tr>
<td>Ho</td>
<td>0.261</td>
<td>0.249</td>
<td>0.025</td>
<td>0.018</td>
</tr>
<tr>
<td>Er</td>
<td>0.755</td>
<td>0.71</td>
<td>0.072</td>
<td>0.051</td>
</tr>
<tr>
<td>Tm</td>
<td>0.102</td>
<td>0.092</td>
<td>0.003</td>
<td>nd</td>
</tr>
<tr>
<td>Yb</td>
<td>0.684</td>
<td>0.628</td>
<td>0.063</td>
<td>0.047</td>
</tr>
<tr>
<td>Lu</td>
<td>0.105</td>
<td>0.096</td>
<td>0.01</td>
<td>0.007</td>
</tr>
<tr>
<td>Y</td>
<td>8.61</td>
<td>9.53</td>
<td>0.98</td>
<td>0.737</td>
</tr>
</tbody>
</table>

Table 3.9 March 2013 rare earth element (REE) assemblages of three LRA sites, and RN downstream of its confluence with the LRA. nd – not detected.
3.4.3 River Cross-Section

The LRA cross section (sample code LRA XS) was measured under the bridge of the road out of the town. Total water flux was 0.63 m$^3$/s.

![LRA Cross Section](image)

**Figure 3.5** River cross-section from the Lower Río Agrio.

3.5 Solid Sample Compositions

<table>
<thead>
<tr>
<th>Sample name</th>
<th>SCHW01</th>
<th>SCHW02</th>
<th>SCHW03</th>
<th>SCHW04</th>
<th>SCHW07</th>
<th>SCHW06</th>
<th>SCHW05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>LRA</td>
<td>Salto</td>
<td>LRA</td>
<td>Salto</td>
<td>LRA</td>
<td>Salto</td>
<td>CVL</td>
</tr>
<tr>
<td>Majors</td>
<td>wt %</td>
<td>wt %</td>
<td>wt %</td>
<td>wt %</td>
<td>wt %</td>
<td>wt %</td>
<td>wt %</td>
</tr>
<tr>
<td>Al</td>
<td>1.03</td>
<td>1.09</td>
<td>1.22</td>
<td>1.21</td>
<td>0.68</td>
<td>1.57</td>
<td>0.16</td>
</tr>
<tr>
<td>Ca</td>
<td>0.1</td>
<td>0.13</td>
<td>0.12</td>
<td>0.15</td>
<td>0.15</td>
<td>0.25</td>
<td>0.16</td>
</tr>
<tr>
<td>K</td>
<td>0.02</td>
<td>0.09</td>
<td>0.01</td>
<td>0.02</td>
<td>0.04</td>
<td>0.16</td>
<td>3.54</td>
</tr>
<tr>
<td>Mg</td>
<td>0.08</td>
<td>0.2</td>
<td>0.1</td>
<td>0.12</td>
<td>0.05</td>
<td>0.69</td>
<td>0.02</td>
</tr>
<tr>
<td>Na</td>
<td>0.02</td>
<td>0.05</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
<td>0.61</td>
</tr>
<tr>
<td>Fe</td>
<td>33</td>
<td>18.7</td>
<td>29.7</td>
<td>28</td>
<td>27.8</td>
<td>2.69</td>
<td>29.5</td>
</tr>
<tr>
<td>S</td>
<td>1.2</td>
<td>1.71</td>
<td>1.36</td>
<td>2.15</td>
<td>2.63</td>
<td>0.35</td>
<td>11.3</td>
</tr>
<tr>
<td>Minors</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
</tr>
</tbody>
</table>
Table 3.10 Major and trace element composition of mud and mineral samples collected 2007-2013. The CVL mud is 0cm depth in the 2004 core. SCHW02 was taken 100m downstream of the Salto del Agrio. nd – not detected.

In the LRA muds, Al is minor element (0.68-1.22 wt%), as is S (1.2-2.6 wt %) and Ca, K, Mg, and Na are trace elements (<<1 wt %). Fe is strongly enriched in LRA mud samples, with 27.8-33 wt% Fe. A sample taken in 2008 100m downstream of the Salto (sample code SCHW02) had slightly less Fe (18.7 wt %). These muds have high levels of As, ranging from 825-1110 ppm, as well as high V (900-1210 ppm) and P (4800-7800 ppm). The 2004 CVL mud core sample (SCHW05) had 2.7 wt% Fe, 1.57 wt % Al, and traces of other RFE; it also had 180 ppm Zn, 68.8 ppm Cu, and 317 ppm Mn. The hydrothermal minerals scraped from rocks near CP had 29.5% Fe, 11.3 % S, 3.54% K,
and minor amounts of Al, Ca, and Na (<1 wt %). It also had high P (3500 ppm) and moderately high As (165 ppm) and Pb (206 ppm).
CHAPTER 4: DISCUSSION OF 2013 RESULTS

4.1 El Vertedero Hot Spring

4.1.1 Major Elements

Between January of 1997 and March of 2013, major element concentrations in El Vertedero hot spring (CP) have varied by up to two orders of magnitude, in conjunction with two eruptive cycles (2000 and 2012) as well as the 2004 thermal anomaly. The volcanogenic elements (VE) $\text{SO}_4$, $\text{Cl}$, and $\text{F}$ varied widely throughout the 2000 and 2012 eruption cycles. The eruption in December 2012 was 21 months after the 2011 samples, and three months before the March 2013 samples, were collected. The sample taken in 2011 has significantly higher concentrations of both VE and RFE compared to the 2013 sample (table 3.1); though fluoride was not detectable in IC analysis of the 2011 sample, several ppm may still be present. In the 24 months between the two samples, sulfate decreased over 62% and chloride decreased almost 93%. Most RFE deceased between 55-69%; the two exceptions were Si, which decreased 42%, and Ca, which decreased only 4%. The pH increased 9.1%, from 1.1 in 2011 to 1.21 in 2013.

Decreased VE and RFE in CP fluids in 2013 relative to 2011 implies either that the chemistry of the subsurface hydrothermal fluids has changed, or they have become further diluted with meteoric water. If this decrease was a result of simple dilution, the ratios between VE and RFE would remain congruent. Whether or not this is the case can be determined by comparing the ratio of RFE concentration (mM) over the respective Cl concentration (mM) in 2011 and 2013. If simple dilution was the culprit for decreased VE and RFE in 2013 CP fluids, RFE/Cl values would remain the same. This is not the case; RFE/Cl values increased dramatically between 2011 and 2013,
indicating an overall reduction in Cl output relative to RFE. S/Cl also increased dramatically, from 1.4 to 7.7 in 2011 and 2013 respectively.

**Figure 4.1** Atomic ratios of RFE/Cl in 2011 and 2013 CP fluids.

Prior to an eruption, heightened concentrations of sulfate and chloride reflect more active input of volcanic gases into the hydrothermal system. The subsequent increase in acidity of the hydrothermal fluids, in conjunction with injection of new magma into the shallow system, would lead to increased water-rock (W/R) interaction and increased concentration of RFE in the hydrothermal fluids. These fluids become saturated and begin to precipitate secondary minerals. Post-eruption, reduced magmatic activity in the shallow hydrothermal system results in reduced VE in the hydrothermal fluids; W/R interaction continues as the fluids become more neutralized, increasing the proportion of RFE relative to VE. The most significant changes in RFE/Cl from 2011 to 2013 are the Al/Cl and Ca/Cl values. Dissolution of secondary Al and Ca species, precipitated before or just after the 2012 eruption, would account for this incongruous increase in Al/Cl and Ca/Cl. Anhydrite (CaSO₄) dissolution could be additionally responsible for the relatively high SO₄ values relative to Cl. (See Chapter 6 for discussion of modeled
saturation results). Oxidation of magmatic H₂S to H₂SO₄ in the shallow hydrothermal system may also be responsible for the increased proportion of SO₄ in the VE assemblage (Kusakabe et al, 2000). Though VE fluxes decreased after the 2012 eruption, residual H₂S in the shallow hydrothermal oxidizing as temperatures decrease and pH increases would bolster the SO₄ concentrations in CP fluids.

Si does not decrease as dramatically as other RFE from 2011 to 2013. Concentrations in hydrothermal fluids are limited by the low solubility of Si in water even at high temperatures; incongruent dissolution and/or reprecipitation of Si species out of the hydrothermal fluids prior to reaching the surface likely limits the concentration of Si in the fluids, regardless of higher concentrations of other RFE. Based on Si solubility limitations, Si concentrations would not be expected to exceed 130-140 ppm in the hot spring fluids at Copahue hydrothermal temperatures (Ouimette, 2000; Varekamp et al, 2001; Verma, 2000), and would decrease substantially as the fluids moved toward the surface and cooled.

Mg can be used as a benchmark for W/R interaction, as it (along with Na) is not likely to reprecipitate into secondary minerals, unlike Fe, Al, Ca, and Si (Varekamp 2004; 2009). Thus, the 54.9% decrease in Mg concentration can indicate decreased W/R interaction as well as dilution by meteoric water. Decreased permeability of the hydrothermal system may also be responsible for a reduction in the export of high-RFE fluids: precipitation of secondary minerals hampers fluid flow and decreases the portion of magmatic fluids in the shallow hydrothermal fluids. Stable water isotope values of the fluids would show the portion of magmatic water in the fluids relative to the local meteoric water line and determine if there was a decrease in magmatic water in the HT fluids between 2011 and 2013.
4.1.2 Trace Elements

High As concentrations in hydrothermal fluids result from extensive W/R interaction at hydrothermal temperatures and redox conditions (Aiuppa et al, 2006), as well as volcanic gases (Agusto, 2013). As and other incompatible elements such as Pb, U and Sr are readily mobilized out of silicate rocks at hydrothermal temperatures (You et al, 1996). The “element transfer ratio” (ETR) from rock to water can be calculated based on the transfer of a conservative element, such as Mg. The ratio of trace element concentrations in CP is taken to their respective abundances in the Copahue rocks, and these ratios are then normalized to the Mg ratio. An ETR > 1 indicates the element is preferentially dissolved from the rock, while an ETR < 1 indicates the element is compatible within the rock and is dissolved at a lower rate than Mg or is removed from the fluid through another process.

![Element transfer ratio (ETR) of trace elements in 2013 CP fluids relative to rock from the 2012 Copahue eruption (Camfield, 2013 data).](image)

**Figure 4.2** Element transfer ratio (ETR) of trace elements in 2013 CP fluids relative to rock from the 2012 Copahue eruption (Camfield, 2013 data).
The ETR of trace elements in 2013 CP fluids shows that Zn, U, Sr and Pb are disproportionately abundant in the fluids relative to the rocks, while Ba, Cu, Co and V are relatively depleted in CP fluids relative to Copahue rocks. The elements with ETR >1 may either be disproportionately dissolved from the source rock, or they may derive from another source, such as magmatic gases that are dissolved in the hydrothermal fluids.

The REE of 2013 CP fluids is strongly enriched in LREE relative to chondrite, and is more steeply enriched than bulk Copahue andesites. HREE show slight depletion, but the slopes of the CP curve and Copahue rock curve are similar for HREE.

Figure 4.3 showing relatively steeper LREE enrichment of CP fluids than Copahue rock fluids when normalized to chondrite. When normalizing CP to chondrite, chondrite values were converted to “parts per 10 million” for easier visual comparison with Copahue rock.

Congruent dissolution of wall rock would result in a slope of 0 for the water/rock curve; the non-linear slope of this line and LREE enrichment relative to the rock
indicates incongruent dissolution of Copahue rock in the fluids. LREE are less compatible in the solid rock, so are more easily dissolved into fluids. A mature protolith that had been exposed repeatedly to acidic hydrothermal fluids would become depleted in LREE, resulting in fluids low in LREE relative to the bulk andesite (Gammons, 2005). The relative positive enrichment of LREE in the 2013 fluids suggests they were interacting with a newly intruded body whose LREE had not been depleted by previous water-rock interaction. When normalized to 2012 rock, 2013 fluids have a slope near to zero from Gd to Lu, indicating roughly congruent dissolution of HREE from rock to fluids (figure 4.3).

4.2 Upper Río Agrio

4.2.1 Major Elements

El Vertedero (CP) is the headwaters of the Upper Río Agrio (URA), from whence it flows down the flank of Copahue to Lake Caviahue (CVL). Along the river’s reach it is joined by several glacial meltwater streams that dilute it slightly. The pH of CP, the headwaters, was 1.21 in March 2013; by the time the URA reached CVL the pH was 2.5. As evidenced by analysis of one of the tributaries (URA 6), though these small streams are near-neutral (pH 6.1), they still bear a signature of hydrothermal fluids. This particular tributary had quite high concentrations of Cl and SO$_4^{−}$—comparable to concentrations in URA samples, but had much lower concentrations of RFE (Table 3.2).

RFE concentrations decreased significantly and incongruently from CP to the URA waterfall, and continued to decline toward the lake outlet. Mg was the most conservative between CP and URA 2, decreasing 3.2%. Other RFE’s decreased between 11.9% (Si) and 60% (Ca). Between URA 2 and URA XS 3, RFE again decreased substantially relative to Cl (~9.4%), as did SO$_4^{−}$, and pH increased from 1.6 to 2.5.
Concentrations of RFE in the URA amounted to 394 tonnes of dissolved rock exported by the river per month in 2013. Along the reach of the URA, S/Cl decreases dramatically from CP to the mouth of the river – from 7.732 to 2.763. S/Cl was lowest at the second cross-section site, where it was 1.196. RFE/Cl show similar trends, though the lowest values are at URA 1, where Cl is much higher than the rest of the river. RFE/Cl increases slightly at the lake exit due to a sharp decline in Cl, not an increase in concentration of RFE. The low RFE concentrations in URA 6 is either due to early precipitation of secondary species in the near-neutral waters, or low initial concentrations at the stream’s source. The source of these fluids is likely a cool, shallow neutral chloride hydrothermal spring rather than directly from the volcano itself.

![2013 URA RFE/Cl](image)

**Figure 4.4** RFE/Cl values of 2013 URA samples. URA 2 is the furthest upstream sample, followed by URA 1, URA 3 and URA 1A/1B.

At the time of sampling (late Austral summer), river water flow was quite low; the second cross section, taken several km upstream of the river delta into CVL, had 0.336 m$^3$/s of water flow. The flow at the mouth itself was not much higher; two sub-
channels combined had a flow of only 0.358 m$^3$/s. This flow rate is not representative of an average annual flow; during the spring snowmelt and rainy season river flow is much higher. A previous model by Varekamp (2008) indicates water flow peaks between 2.9 and 3.3 m$^3$/s during the spring. The water flow rate does not impact the absolute flux of VE and RFE through the river, as the input of these elements is volcanic in origin and can be assumed to be independent of dilution by meteoric water. The measured water flux data in conjunction with water VE/RFE concentrations gives the absolute mass export of each element. Total export of major elements was 1,372 tonnes/month using March 2013 concentrations. The Copahue system is highly dynamic; thus these measurements cannot accurately represent element fluxes on a month-to-month basis, but because field work over the 16-year sampling period was almost always performed in late summer, comparisons can be made on a year-to-year basis.

4.2.2 Trace Elements

REE in the URA are similar to REE in CP, though the Eu* of the URA decreases from CP to the two cross section locations (URA XS 3, URA 1A, URA 1B). CP fluids have a relatively less negative Eu anomaly due to dissolution of plagioclase in the fresh protolith within the hydrothermal system – Eu is preferentially taken up in plagioclase, and plagioclase is relatively more easily dissolved in W/R interaction than mafic minerals (Bau, 1991). In the URA, dissolution of riverbed rocks that have already undergone extensive W/R interaction would lead to a more negative Eu anomaly, as other REE became more abundant and the Eu in those rocks would have already been extracted.

Like CP, trace metals in the URA derive from W/R interaction, as well as dissolved volcanic gases. Trace metals in the URA are not congruently diluted from CP levels, as a
result of continued W/R interaction and tributary mixing along the river’s reach. As the URA is diluted from its original CP waters, trace metals are likely being added either from a secondary stream source, such as the hydrothermally-enriched meltwater streams, or are being dissolved from rocks in the riverbed. Concentrations of more compatible elements do not decrease as strongly from CP to the URA because extensively altered riverbed rocks have already lost a disproportionately large amount of incompatible elements.

4.3 Lake Caviahue

4.3.1 Major Elements

CVL has overall lower RFE/Cl values than URA 1A/1B. CVLSBB has higher average RFE/Cl than the other profiles, indicating it is most similar in composition to the URA and therefore the “youngest” lake water. In CVLSAA and CVLSBB, the increase in concentration of with depth of several RFE (Na, Mg, Ca, Fe) suggests a plume of more dense, concentrated water from the URA outlet. The CVLS profiles maintain similar concentrations for all elements, indicating that the southern arm of the lake is more well-mixed relative to the northern arm. It takes 40 months for CVL to echo changes in CP fluid concentrations and element ratios (see Chapter 5) – close to one water residence time of 42 months – thus the VE and RFE signature in CVLS in March 2013 would represent inputs from 2009-2010.

CVLNAA is slightly more depleted in most of the RFE, except for Al. Increased Al in CVLNAA may be attributed either to an earlier high flux of Al prior to or during the December 2012 eruption, or to another source such as the Agua Dulce or the town’s wastewater. Based on prior monitoring of URA fluxes before, during, and after eruptions (Varekamp, 2009), the former is most likely: post-eruption, there was a sharp
decrease in Al flux between December 2012 and March 2013, accounting for the
difference between CVLNAA and CVLNBB. (See Appendix B for all CVL depth
profiles).

4.3.2 Trace Elements

Hydrothermal contamination of CVL water from the URA results in abundant trace
mets in CVL; many exceed WHO standards for safe drinking water (As, Pb especially).
CVL trace elements are diluted from original CP values; based on Mg concentrations in
CVL relative to CP (Mg being used as a baseline conservative element) the hydrothermal
contaminants are diluted by a factor of 0.09-0.1 in CVL relative to CP. The element
transfer ratio (ETR) used to compare CP fluids to Copahue rocks can be applied here to
compare the transfer of trace elements from CP into CVL (figure 4.5). Mg is again used
as a reference for conservative behavior. Co, Ti and Ni are close to conservative, while
As, P, Cr, Cu, Ga, Zn, U, V, Th, Sr, Rb, Sc, and Pb are depleted in CVL relative to CP.
Li is enriched in CVL relative to CP. There is very little variation along the depth profile.

Figure 4.5 Element transfer ratio (ETR) of CVL trace elements relative to CP
abundances. ETR is normalized to Mg, assuming conservative behavior of Mg.
The depletion of As, P, Pb, and other trace metals relative to CP abundances may result from precipitation of secondary phases in the lake; in 2013 CVL was saturated in SiO$_2$ and several Fe-oxides and Fe-hydroxysulfates including schwertmannite (Chapter 6). The schwertmannite preferentially incorporates As and V, while it does not impact divalent trace metals like Co and Ni.

The REE signature of CVL is very close to URA trends: La/Sm is only slightly higher than URA, while LRA and CP are much higher. Eu* in CVL water is somewhat higher than URA values.

**Figure 4.6** REE/Chondrite of CP, URA 3, average CVL and LRA SdA, 2013 values.

The REE values for the 2013 CVLS profile vary slightly by depth. When the REE of the five samples and their average are plotted simply normalized to chondrite, variations are almost impossible to discern. However, when these normalized values are normalized again to their average, trends become more clear (**figure 4.7**): 0m is relatively depleted in La-Sm relative to the other depths, but becomes enriched Eu-Lu. The 15m
sample is the most enriched overall relative to the other profiles, at about 1.05x the average value. 30m is slightly depleted throughout the whole suite of REE, except for La, Eu, and Yb where it is equal to or slightly above the average. 45m is close to average for La-Sm but then rapidly becomes much more depleted Eu-Lu (about 0.95x the average). The 60m sample is just above average in La, and decreases slowly along the series toward more depleted values. La/Sm is slightly lower in the 15m sample (3.69) relative to the others (3.80-3.95).

**Figure 4.7** CVLSA profile rare earth element (REE) values, normalized to the average of the whole profile. Dashed line is equal to average/average – values above this line are enriched relative to the average; values below are depleted.

4.4 Lower Río Agrio – Water and Mud

4.4.1 Major Elements

The decrease in concentrations of VE and RFE from the LRA lake outlet toward RN can be attributed both to dilution of contaminated waters with freshwater tributaries,
as well as precipitation of secondary minerals. Between the cross-section (LRA XS) and the SdA field sites, the riverbed became coated with red oxide minerals and algae. Between the lake outlet and the Salto del Agrio (SdA), pH increased from 2.9 to 3.5; this transition creates more favorable conditions for the precipitation of iron oxides and hydroxides such as hematite (Fe₂O₃), goethite (FeO), and schwertmannite (Fe²⁺₈(OH)₆(SO₄)₈nH₂O or Fe³⁺₁₆O₁₆(OH, SO₄)₁₂.1₃•10-12H₂O). Schwertmannite is a metastable iron-oxyhydroxysulfate mineral that is ubiquitous in acid-sulfate drainages and is the dominant species at pH values between 2-4; at higher pH ferrihydrite and goethite are the dominant minerals (Bigham et al, 1996). It precipitates in supersaturated acid solutions as Fe(II) oxidizes to Fe(III); if left to react the solution will neutralize and the schwertmannite will transform into goethite and some jarosite, eventually becoming exclusively goethite (Acero et al, 2006). However, as the LRA ocher mud receives a constant input of acid-sulfate water, it is not likely that the schwertmannite turns to goethite.

Gammons et al (2005) found that Fe speciation in LRA waters was over 90% Fe³⁺ in 2003, consistent with conditions ideal for schwertmannite precipitation; concentrations of RFE at that time were higher and pH was lower, so it is likely that the more neutralized 2013 samples had at least as much Fe³⁺ relative to Fe²⁺. LRA waters were depleted in Fe and Al, and SO₄, consistent with precipitation of schwertmannite, goethite, and jarosite, with some alunite possibly in solid solution with jarosite. The ocher mud from LRA was mainly Fe, with some Al and S, and very low levels of other RFE present in the LRA water; the large proportion of Fe in the mud is consistent with the stoichiometric abundance of the Fe²⁺ polymorph of schwertmannite, as well as goethite.
4.4.2 Trace Elements

The ocher mud composition was consistent with schwertmannite, especially as it contained high levels of As, V, and P, while the LRA SdA water was depleted in both major and trace elements associated with schwertmannite. When schwertmannite precipitates it selectively removes As from the solution but leaves other trace metals relatively unchanged (Acero, 2006). The ocher mud compositions reflect this selective uptake; they have high levels of As, V, and P and low levels of the above trace metals; LRA trace metal compositions reflect this trend: strongly decreasing As and V, while other trace metals remain higher. While small quantities schwertmannite may be dissolving as new acidic water reacts, it appears that precipitation of new ocher dominates the reaction and thus continually depletes As and V from the fluids.
CHAPTER 5: TIME TRENDS 1997-2013

This chapter will compare the data available for CP, URA and CVL for the period 1997-2009 from earlier studies (Agusto et al. 2012; 2013; Gammons et al, 2005; Geller et al, 2006; Ouimette, 2000; Varekamp et al, 2001; 2003; 2004; 2008; 2009) and insert the new 2013 data (and 2011 where applicable) into this time series. The compositional and elemental flux trends during the last two eruptions (2000 and 2013) will be compared; the respective similarities to the reaction of the hydrothermal system to the volcanic activity will be explored. In all these comparisons, dilutions of the CP fluids (and possibly in the underlying hydrothermal fluids) and in the URA fluids play a major role in the absolute concentrations that were observed. For that reason, element ratios and their trends over time will be emphasized, to eliminate the dilution component. Mixing proportions of hydrothermal fluids and meteoric waters are unknown for the 2013 samples, as $\delta^{18}O$ data has not yet arrived (samples are still at Yale University to be analyzed); thus absolute conclusions cannot be drawn about the dilution in 2013 samples. All figures in this section are marked with vertical red lines to indicate the 2000 eruption (43 months), 2004 “thermal anomaly” (87 months), and 2012 eruption (192 months).

5.1 El Vertedero (CP)

5.1.1 Major Element Trends

Sulfate and chloride concentrations were highest in the years leading up to the 2000 eruption: both were highest in 1997, with 64,240 ppm SO$_4$ and 10,617 ppm Cl. Concentrations of Cl and SO$_4$ decreased steadily from March 1997 to November 1999. Syn-eruptive samples taken in July of 2000 show increased VE (figure 5.1) relative to November 1999 samples. Post-eruption concentrations of all three decreased
substantially by January 2001; SO$_4$, Cl and F decreased approximately 40%, 50% and 70% respectively. This is mostly the result of dilution inside the hydrothermal system: pH increased, the fluxes decreased, and most likely the ratio between meltwater and hydrothermal water decreased as the permeability in the deep hydrothermal system decreased. The trends in absolute VE concentration of the hydrothermal fluids can be observed by dividing the observed CP concentrations by the fraction of andesitic water (AW) – this fraction is calculated from the $\delta^{18}$O and $\delta$D values of CP fluids relative to the local meteoric water line (figure 5.2). This method corrects for the dilution effect and shows absolute trends in the hydrothermal system. Using available AW fraction data from 1997-2008, CP concentrations of VE are normalized to the AW fraction in figure 5.3.

Figure 5.1 SO$_4$ and Cl concentrations (ppm) in CP fluids, 1997-2013.

Absolute concentrations of SO$_4$ continued to decrease until March of 2004, when an increase of $\sim$4500ppm occurred between February 2003 and March of 2004. Cl and F concentrations increased between January 2001 and March 2004; F peaked in March 2002 at over 1200ppm. Following high concentrations in March 2004, values for all VE
decreased rapidly, with similar magnitudes as post-eruptive drawdown in 2001. From 2006 to 2011, concentrations again climbed and stabilized for several years.

Cl and SO$_4$ behave similarly only from 1997 to 2001; the system is recharged with Cl through 2004 while SO$_4$ continued to decline. The increased Cl flux during that time period, along with increased concentrations of RFE in 2004, suggests heightened hydrothermal activity, despite no eruption. The S/Cl of CP decreases after the 2000 eruption and remains relatively low until the 2012 eruptive cycle. Declining SO$_4$ post-eruption is likely related to the precipitation of sulfate minerals including anhydrite and alunite within the hydrothermal system, while Cl remains conservative as it travels through the hydrothermal system to the surface. The dramatic increase in S/Cl during the 2012 eruption is likely due to both increased flux of volcanogenic sulfate, as well as dissolution of sulfate precipitates within the shallow hydrothermal system.

![CP fraction of Andesitic Water 1997-2008](image)

**Figure 5.2** Fraction of andesitic water (AW) 1997-2008; data from Varekamp (unpublished)
Figure 5.3 F, Cl and SO₄ concentrations in CP normalized to the fraction of andesitic water (AW), giving the concentrations in the hydrothermal fluids prior to dilution.

When normalized to fAW, the trends in VE concentration in hydrothermal fluids become more congruent throughout the eruptive cycles. The 2000 eruption saw a rapid increase in VE concentrations, which then attenuated over the next three years. SO₄ decreased to below pre-eruptive levels by 2003, while Cl recovered to a similar or slightly elevated concentration. F increased during the eruption and remained at that level for the next four years. In 2004 there was a small spike in VE output followed by rapid decrease; VE then recovered to greater than previous concentrations and remained relatively stable for the next several years. The relatively stable fluctuations in the fAW-corrected VE concentrations shows the impact that dilution has on VE and RFE concentrations in CP. Changes in VE and RFE concentrations are thus a result of both changes in the hydrothermal fluid concentration and changes in permeability of the hydrothermal system.
The atomic ratio of S/Cl is another way of subverting the dilution effect in CP fluids to observe relative trends (figure 5.4): the relatively constant S/Cl for the first 43 months (pre-eruption) indicates change in concentrations was due to dilution. A small uptick in S coincided with the arrival of new magma in 2000. Over the next three years S decreased due to precipitation of alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) and anhydrite ($\text{CaSO}_4$) in the reservoir (see Chapter 6 for saturation modeling). The system is then in near steady-state from 2006-2011, at which point S/Cl increases precipitously. The increase of other RFE/Cl values and relative decrease in Cl values indicates there was overall less Cl in the hydrothermal system starting in 2011.

RFE concentrations fluctuate incongruently throughout the timeline. Al and K are coupled throughout the eruptive cycles, likely as a result of alunite precipitation and re-dissolution throughout the eruptive cycles. Ca does not correlate strongly with other RFE. Mg, Na and Fe appear to behave relatively conservatively; fluctuations in the

Figure 5.4 S/Cl (mM values) of CP fluids 1997-2013.
concentrations of these RFE are likely largely the result of dilution of the hydrothermal fluids.

**Figure 5.5** Concentrations of Ca, Al and K in CP over time.

**Figure 5.6** Concentrations of Fe, Mg, and Na in CP fluids from 1997-2013.

K and Al are strongly correlated over time but do not correlate with conservative elements Mg and Na, suggesting K and Al are precipitating congruently in a secondary species. Saturation models (Chapter 6) indicate saturation of alunite in the
hydrothermal system during eruptive events; precipitation of alunite is visible in CP through the congruent behavior of Al and K. K/Cl and Al/Cl correlate strongly throughout the eruptive cycles (figure 5.7). Prior to the 2000 eruption K/Cl and Al/Cl increase, possibly due to dissolution of alunite as acidity increases. With the arrival of new magma, alunite becomes saturated and Al and K are removed from the hydrothermal fluids along with SO$_4$ (figure 5.4) until relative steady-state is reached in 2002. Slight increase in 2004 can be linked to the small-scale increase in acidity from the thermal anomaly; small amounts of alunite dissolved and Al and K were released.

![Al/Cl and K/Cl of CP fluids, 1997-2013](image)

**Figure 5.7** Al/Cl and K/Cl of CP fluids from 1997-2013.

### 5.1.2 Trace Element Trends

Rare earth elements (REE) in CP fluids are generally enriched in LREE relative to HREE for all years. The slope of LREE enrichment (La/Sm) varies over time; it is generally higher following eruptive activity. The LREE are more incompatible than HREE, so if they were abundant in the protolith they would be slightly more preferentially leached relative to HREE. Enrichment in LREE with a high La/Sm indicates the fluids had been undergoing W/R interaction with a new protolith that had
not been previously depleted in LREE; this may be new magma injected into the shallow hydrothermal system prior to or during an eruption. W/R interaction with new magma is easily visualized when the La/Sm ratio of CP fluids is normalized to the La/Sm of bulk Copahue andesite and plotted over time (“La/Sm norm”, figure 5.8). When this ratio >1, LREE are enriched in the fluid relative to rock. There are three significant groupings in LREE enrichment over time, divided by eruptive activity. Prior to the 2000 eruption, CP was enriched in LREE relative to the rocks, though this ratio decreased rapidly from 01/1999 to 11/1999. Following the 2000 eruption, the La/Sm norm increased, peaking in 2003. The 2004 thermal anomaly marked a rapid decrease in La/Sm norm, and the fluids were depleted in LREE relative to rock from 11/2004 onward, until it became enriched again in 2013. The decrease in 2004 is likely a result of accelerated W/R interaction from increased acidity, without input of fresh magma. The protolith in the hydrothermal system became rapidly depleted in LREE, and the fluids remained depleted until new magma was intruded during the 2012 eruption.

![La/Sm norm: (La/Sm)$_{CP}/$(La/Sm)$_{rock}$ 1997-2013](image)

**Figure 5.8** La/Sm norm from 1997-2013 in CP fluids relative to bulk Copahue andesite.
Trace elements in CP fluids fluctuated significantly throughout the eruptive cycles. Dilution effects added noise to the time trends of CP concentrations, so again the fraction of magmatic water is employed in figure 5.9 to examine fluctuations in V, As, and Ni. While Ni is mostly dissolved during W/R interaction, V and As may enter the fluids in dissolved magmatic gases. After the 2000 eruption, the fraction of magmatic water in CP decreased to 13.6% in 2001; normalized concentration of all three elements increase dramatically that year and attenuate for the next 36 months. The small fraction of magmatic water indicates the permeability of the hydrothermal system had been plugged up since the 2000 eruption, when magmatic water was 66% of CP fluids. During the 2004 thermal anomaly, Ni remains relatively unchanged compared to V and As, which may have entered the hydrothermal fluids with increased magmatic gas flux. As and V increase again in 2006; at this time the fraction of andesitic water is relatively low in CP (31%), so while there may have been increased fluxes of volcanogenic elements in the hydrothermal reservoir, decreased permeability diluted the fluids and the increased flux was not seen at the surface.

![V, As, Ni normalized to fAW](image)

**Figure 5.9** V, As, and Ni concentrations in CP normalized to the fraction of andesitic water, giving the concentration in unmixed hydrothermal fluids.
5.2 Upper Rio Agrio (URA)

Absolute concentrations of VE and RFE in the URA are dependent not only on volcanic inputs, but also on seasonal water flow rates. As a result, concentration data obtained only once in a given year does not yield useful information about the URA’s transport of VE and RFE unless it is normalized to a conservative element such as Cl. With water flow data for each sampling period, the absolute quantity of VE and RFE that is exported per month can be estimated using the concentration data and water flow rate. The most notable variations in element fluxes in the URA are seen surrounding the 2000 eruption (Fig. 5.10). Fluxes of all VE and RFE increase prior to and during the 2000 eruption, and then undergo a period of decreased flux from 2001 to 2003.

![Fluxes of VE and RFE in URA 1997-2013](image)

**Figure 5.10** Mass fluxes of volcanogenic elements and rock-forming elements in the URA, 1997-2013

These temporal changes in volcanic fluxes occur rapidly, so in later years when data were not collected (2005, 2007, 2010, and 2012) there may have been temporary changes in volcanic fluxes that were not seen. Similarities between the 2000 and 2012 eruptions...
suggest there was a similar spike in volcanogenic flux during the 2012 eruption. The ubiquitous decrease in volcanic flux following the 2000 eruption can be attributed to decreased permeability of the hydrothermal system, as a result of secondary precipitation of alunite and anhydrite. Fluxes of Al and K decrease sharply following both eruptions; from 2000-2002 there is a 6-7-fold decrease in fluxes. Again from 2009 to 2013, fluxes nearly shut off – there is a 5-6-fold decrease in Al and K, and most VE and RFE are at all-time low fluxes in 2013.

5.3 Lake Caviahue (CVL)

Due to its large volume and long water residence time (42 months), CVL acts as a reservoir for VE and RFE long after fluxes have changed. Concentrations of Cl and \( \text{SO}_4 \) in CVL are somewhat inversely related to pH in the lake: as VE concentrations increase, pH decreases. This trend is most clear throughout the 2000 eruptive cycle – the lake was rapidly acidified as concentrations of VE increased, even as RFE concentrations increased as well (Fig. 5.11, 5.12). After 2004, the pH of CVL rose rapidly, peaking at 2.86 in 2011. pH continued to rise despite increasing VE in from 2009-2011, likely as a result of higher overall neutralization of hydrothermal fluids from heightened RFE concentrations: as long as H\(^+\) is consumed during W/R interaction, the pH will not be reduced by increased anion concentrations in the lake. This accounts for the continually climbing pH from 2008-2011 despite increased VE concentrations. The pH of CP fluids was higher in 2006-2013 than it had been in previous years; the lake was therefore less acidified.

RFE concentrations show more complex time trends in CVL (Figure 5.11). While basic trends of increased concentration during eruptive periods are visible, there is not congruent decrease of RFE following eruptive periods. Al and K show a general
Figure 5.11 pH and VE concentrations in CVL 1997-2013. There is an inverse correlation between pH and concentration of VE in CVL.

Figure 5.12 Major RFE concentrations in CVL 1997-2013. Note similar trends of Al and K.
correlation following the 2000 eruption, though they are not as closely linked as in CP fluids. CVL may receive additional RFE from sediment loads from the URA and Agua Dulce. Sedimentation within the lake likely plays a role in the incongruent life cycles of RFE in the lake.

5.4 Lower Rio Agrio

Element concentrations in the LRA are closely related to CVL concentrations, as it flows directly from the lake. Precipitation of schwertmannite, hematite, jarosite, and SiO$_2$ species results in decreasing Fe concentrations down the reach of the river. When CVL has a lower pH, the LRA does not precipitate these minerals as readily and its composition remains relatively congruent as it flows toward the Río Norquín.
CHAPTER 6: AQUEOUS GEOCHEMICAL MODELING

6.1 Summary of Modeling Procedure

WebPHREEQ allows for near-instantaneous calculation of complex geochemical processes and easy manipulation of environmental conditions. Thus, modeled saturation indices may be calibrated using known field measurements and observations. At the Copahue-Caviahue watershed, native sulfur was ubiquitous in the upper watershed and summit crater; thus when using CP data in WebPHREEQ models, redox conditions (pe) were manipulated such that native sulfur was saturated. At the relatively low pressures in the hydrothermal reservoir and surface hot spring, native sulfur is stable only within a narrow window of pe values – approximately between 0 and 3 (Church et al, 2007). Accordingly, estimated pe values used for our WebPHREEQ models were between 1 and 3. The simple speciation program was used for all runs in this study.

The speciation models for CP data were calculated using selected pre- and post-eruption years, each run at four static temperatures. Data sets from 1997, 1999, 2000, 2002, 2011 and 2013 were each run at 70°C, 120°C, 180°C and 230°C, to represent a range of temperatures present in the hydrothermal system. The 230°C maximum was selected based on previous calculations of quartz temperatures, which range between ~170°C before the 2000 eruption and up to nearly 250°C after the eruption (Varekamp et al, 2004). The hydrothermal reservoir's maximum temperature was previously calculated using the S isotope equilibrium between S⁰ and SO₄, yielding a maximum of 300-350°C, at a minimum 1500m depth (Ouimette, 2000; Varekamp et al, 2004; Varekamp et al, 2009). 230°C was selected because while the unaltered hydrothermal fluids may originate at higher temperatures, mineral saturation in the shallow, cooler
For CVL fluids, two compositions from each study year between 1997 and 2013 were run at the field temperature; pe = 15. As there are a large number of samples for each year from CVL, demonstrating a range of concentrations within the lake, the samples selected for WebPHREEQ runs were the overall maximum and minimum values for that given year. The goal of this method is to determine the range of saturation indices possible throughout the lake. Individual sample location was not considered in selecting each pair of samples, as location data did not accompany all of the samples from previous years.

6.2 Limitations of WebPHREEQ and this dataset

WebPHREEQ allows for inputs of six environmental conditions, only two of which were measured in the field. Oxidation state (pe) had to be estimated based on field conditions and element concentrations; density, pO_2 and pCO_2 were left blank. Atmospheric values of pO_2 and pCO_2 could have conceivably been used for CVL samples, though this would be representative only of surface waters and not the entire water column. pO_2 and pCO_2 of CP fluids are unknown but pe is approximated based on field observations. Saturation modeling was not useful for the URA, as even in March, when water flow is lowest and the fluids are thus the most concentrated, a trial WebPHREEQ run indicated that the fluids are not saturated in any minerals.

While bulk concentrations of all major elements were available for all samples, additional information that may have affected speciation was not available: Fe speciation and F concentration (some samples). Additionally, the thermodynamic data used in the program may not be entirely representative of the empirical range for a given mineral
species. WebPHREEQ is a greatly simplified version of the desktop program PHREEQC, so computing power may be limited. For the purposes of this study – determining mineral saturations of single solutions at a given set of conditions – WebPHREEQ proved to be a sufficient tool.

6.3 Modeling Copahue’s hydrothermal system via El Vertedero

As the most concentrated and acid hot spring, CP fluids most closely represent the geochemistry of fluids within the hydrothermal system. δ¹⁸O and δD values of CP water indicate that it is made up of 50-70% magmatic water (lower after eruptions), which has mixed with local groundwater (figure 5.2, Ouimette, 2000; Varekamp et al, 2001). The fluids have undergone W/R interaction with a protolith within the hydrothermal system, resulting in high concentrations of dissolved RFE. As concentrations of these RFE increase in the fluids, and as the acids in the fluids begin to become neutralized, secondary phases become saturated and precipitate from the fluids. The phases that become oversaturated may be constrained to certain temperature and pH windows; phases that are oversaturated at hydrothermal temperatures and low pH may become undersaturated at lower temperatures, and thus not be observed in the field as secondary precipitates at the hot spring exit point. Using the analyzed waters from pre- and post-eruptive years, as well as one syn-eruptive sample (July 2000), WebPHREEQ allows for calculation of mineral saturations at hydrothermal temperatures as well as surface temperatures.

6.3.1 Results of CP models

By using water chemistry data for the 2000 and 2012 eruption cycles, as well as syn-eruptive data from 2000, changes in hydrothermal mineral saturation can be predicted.
Figure 6.1
Native sulfur (S) and pyrite (FeS$_2$) were oversaturated for all years and most temperatures, except for the undersaturation of pyrite in 2002 at 230ºC. Given the especially high abundance of sulfur species in the Copahue system, saturation of sulfur phases is ubiquitous in the concentrated fluids (Varekamp et al, 2004). At 180ºC, pyrite is oversaturated between 1997 and 2000, and but smaller SI values prevail from 2000 to 2011, increasing slightly again in 2013; native sulfur follows this same trend but with smaller magnitude variations in SI. This is the only temperature where sulfur and pyrite show opposing trends to the other minerals. Goethite (Fe$^{2+}$O(OH)), is always undersaturated – at an SI of approximately -5 – for all years. Anhydrite (CaSO$_4$) shows temperature-dependent saturation: the saturation index of anhydrite increases for all years with increasing temperature, becoming oversaturated at 180ºC in 1997 and 2011.

Anhydrite is mostly saturated in 1997 and 2011-2013, decreasing from 1999 to 2002. Several SiO$_2$ species (quartz, chalcedony, amorphous silica) remain close to saturation or oversaturated through all years.

At 230ºC anhydrite is continuously oversaturated for all years. Alunite (KAl$_3$(SO$_4$)$_2$(OH)$_6$) and jarosite (KFe$^{3+}$_3(SO$_4$)$_2$(OH)$_6$) are strongly correlated in saturation over time and temperature. Jarosite has large negative SI values compared to alunite, but trends are closely mirrored in slope. Alunite becomes saturated at 120ºC in 2011 and 2013; it remains close to or above saturation for those years at higher temperatures. Saturation is lowest in 1999 and 2002; SI increases for all years with increasing temperature: SI of alunite ranges from -33.22 (2002) to -11.7 (2013) at 70ºC for all years, while the window at 230ºC is -2.15 (1999) to 1.64 (2011). Jarosite is still undersaturated, but is closer to saturation at higher temperatures as well. At 70ºC its SI ranges between -55.89 (1999) and -34.15 (1997); at 230ºC the overall range is more positive, between -
23.78 (1997) and -22.68 (2000). The highest SI values are obtained for both alunite and jarosite in 1997 and 2011-2013, though there is also consistently a small peak in 2000 for all temperatures.

### 6.3.2 Discussion

Minerals whose saturations in hydrothermal fluids respond most strongly to fluctuations in VE and RFE concentrations throughout the eruptive cycle tend to be sulfate minerals with significant RFE components. Anhydrite, alunite, and jarosite contain major rock-derived elements (K, Al, Fe) as well as sulfate. While minerals with other sulfur valences, like native S\(^0\) and pyrite (Fe\(^{2+}\)–S\(^2\)-–S\(^2\)-), show consistent oversaturation throughout the eruptive cycles, sulfate minerals show dynamic changes in saturation that can be correlated across the two main eruptive cycles. Fe\(^{2+}\) species (pyrite, pyrrhotite, mackinawite) have higher SI than Fe\(^{3+}\) species (jarosite, goethite, hematite), likely as a result of reducing conditions within the system.

Jarosite remains well undersaturated; at the low \(p_e\) values in the hydrothermal system jarosite is generally stable at higher pH. Additionally, low quantities of ferric relative to ferrous iron in the hydrothermal fluids (Gammons, 2005) decrease the available Fe\(^{3+}\) for jarosite saturation. The saturation model results suggest that alunite dominates within the hydrothermal system. Brophy et al (1962) find that at higher experimental temperatures and pressures (150ºC and 6.1 atm), the preferential incorporation of Fe\(^{3+}\) in the alunite-jarosite crystal structure decreases, leading to increased Al taken up in the alunite-jarosite solid solution. Those experimental data agree with this study’s WebPHREEQC model results of higher SI values for alunite relative to jarosite in these hydrothermal fluids.
Intrusion of new magma into the shallow hydrothermal system prior to an eruptive event would result in an increased flux of acidic magmatic fluids, which undergo W/R interaction with the new protolith, allowing for dissolution of large quantities of RFE into the hydrothermal fluids. As these fluids continue to undergo W/R interaction, alunite and anhydrite become oversaturated and precipitate, decreasing the permeability within the hydrothermal system. Decreased permeability is evidenced by rapid decreases in VE and RFE fluxes in CP within 3-6 months after both the 2000 and 2012 eruptions and decreased portion of magmatic water in CP fluids (Figure 5.2). Modeled SI of alunite in 2000 at 230ºC predicts that alunite was not saturated during the 2000 eruptive cycle at that temperature, though its SI approached 0 in 2000. Nonetheless there is a strongly correlated decrease in Al/Cl and K/Cl following the 2000 eruption (figure 5.7). The closely correlated relationship of Al and K throughout all years suggests there is alunite precipitation occurring. To determine if temperature was a limitation, the 2000 data were re-run at the same conditions but with varying high temperatures to determine if higher temperatures led to oversaturation of alunite. There was a dramatic transition from negative SI at 370ºC to high positive SI at 375ºC – alunite SI was 19.49, and anhydrite SI was 10.19. Also saturated were Al(OH)$_3$ (a), pyrrhotite/mackinawaite, fluorite, gibbsite, gypsum, pyrite, and native sulfur. The results of this model run suggest that rapid heating of the hydrothermal system during an eruption would lead to significant oversaturation of alunite and subsequent precipitation. The decreased permeability of the system following the eruption – as indicated by the fraction of magmatic water in CP – supports the notion that alunite precipitates out during an eruption and plugs the pores of the system, decreasing permeability.
6.4 Modeling Saturation in Lake Caviahue

WebPHREEQ was used to model mineral saturation in Lake Caviahue at field temperature and pH values. Two models were run for each year that data were collected; two samples per year were selected to represent the highest and lowest range of concentrations for that year. The chemical composition varies with depth and with location in the lake, so this method gives a best estimate for the range of saturation indices in a given year. An estimated \( pe \) value of 15 was used for all model runs – close to, but slightly more reducing than atmospheric \( pe \) \( (18) \) – as Gammons et al (2005) found that Fe speciation in CVL was almost entirely \( \text{Fe}^{3+} \) with \( \text{Fe}^{2+} \) increasing toward the surface. Some sample years were not analyzed for Si, so the SI of silica species is not available for all years.

6.4.1 Results of CVL Models

Quartz and chalcedony (\( \text{SiO}_2 \)) were above saturation for all years, and amorphous \( \text{SiO}_2 \) was close to saturation. The SI values for these mineral phases showed no significant trends over time. Hematite (\( \text{Fe}_2\text{O}_3 \)) and goethite were oversaturated for all years; the SI of goethite ranged from \(~2\)\(-5\), while the SI of hematite was between \(~6\)\(-10\). Jarosite was undersaturated from 1997\-2002; in 2002 and 2003 it became briefly saturated before decreasing by 2004. It became saturated again for the “low” values model in 2006, though the “high” values model remained undersaturated until 2009, when both models increased sharply to oversaturation from 2009 to 2013. The SI of jarosite was lowest in 2000, 2004 and 2008 (low concentration model). The saturation index curves for goethite and alunite are closely correlated with that of jarosite; these three minerals exhibit similar changes in saturation index over time. Alunite ranges between \(-8.9 \) (2004) and \(-4.0 \) (2011). Anhydrite is slightly undersaturated for all years, showing strong peaks.

**Figure 6.2** Saturation indices of alunite in CVL for high and low value WebPHREEQC runs, 1997-2013 data.

**Figure 6.3** Saturation indices of K-jarosite in CVL for high and low value WebPHREEQC runs, 1997-2013 data.
Figure 6.4 Saturation indices of anhydrite in CVL for high and low value WebPHREEQC runs, 1997-2013 data.

Figure 6.5 (bottom) Saturation indices of goethite in CVL for high and low value WebPHREEQC runs, 1997-2013 data.
6.4.2 Discussion of CVL model results

The SI of anhydrite increases directly before and during eruptive periods, suggesting that increased fluxes of VE and RFE into the lake prior to an eruption lead to increased anhydrite saturation. This increase in anhydrite saturation is negatively correlated with the pH of CVL: pH decreases in CVL as the SI of anhydrite increases. As the lake becomes more acidified and concentrated leading up to an eruptive event, the SI of anhydrite becomes less negative. These correlations are strongest for the 2000 eruption, though it is possible that if data had been collected in December 2012 close to the time of the eruption, there would be a similar spike in acidity in the lake as in 2000. Ultimately anhydrite is never saturated in CVL.

Alunite, jarosite and goethite all show similar saturation trends throughout the timeline. All species experience a drop in saturation as pH decreases in 2000. Saturation in these minerals is positively correlated with the pH of the lake; SI increases with pH. Jarosite becomes saturated in years that the pH is above ~2.6. Alunite remains well undersaturated throughout the timeline, but correlates strongly with jarosite as these two minerals have similar solubility character. While the environmental conditions of CP fluids were more favorable to saturation of the alunite due to high temperatures and low pH and $pe$, in CVL the lower temperature with higher pH and $pe$ are favorable to jarosite saturation. So in conclusion, if any mineral is saturated in CVL it is a mixture of the Fe oxides and jarosite, and unlikely to be anhydrite or alunite.

6.5 Lake Caviahue and Lower Río Agrio Schwertmannite Saturation

Schwertmannite is an iron-oxyhydroxysulfate mineral commonly found in acid drainages (Acero et al, 2006; Bigham et al, 1996). It is a major constituent of the ocher precipitates intermittently found on the LRA riverbed (Kading, 2010). Schwertmannite
has a variable stoichiometry ranging between \( \text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)\cdot n\text{H}_2\text{O} \) and \( \text{Fe}_{16}\text{O}_{16}(\text{OH,SO}_4)_{12-13}\cdot 10-12\text{H}_2\text{O} \); it forms through bacterial oxidation of \( \text{Fe}^{2+} \) to \( \text{Fe}^{3+} \) (Regenspurg et al, 2004). Schwertmannite is a major precipitate in acid drainages with pH values between 2.8 and 4.5, while higher pH drainages are dominated by ferrihydrite and goethite (Bigham et al, 1996). The ocher precipitates found in the LRA riverbed have appeared and disappeared over the sixteen year study period, probably as a result of changes in pH and concentration in CVL and LRA (Kading, 2010; Varekamp, personal communication). In the field, the riverbed was stained orange further upstream in years when the river water and lake water had higher pH values, while a lower pH value in CVL, and subsequently LRA, was associated with the ocher only visible further downstream, or not at all. Modeling the schwertmannite saturation in CVL and LRA fluids over time provides insight into the precipitation and redissolution of these ocher deposits in the LRA; however available aqueous speciation software does not include schwertmannite data.

Using speciation model results from Geochemist’s workbench, Kading (2010) developed a model for schwertmannite saturation in CVL and LRA fluids using the ion activities for \( \text{Fe}^{3+} \), \( \text{SO}_4^{2-} \) and \( \text{K}^+ \), as well as the pH, for 1997-2009 data. For this study, Kading’s model was used, and activities of the various ions were derived from WebPHREEQ models using 2011 and 2013 CVL data, as well as 2013 LRA data. The model results show a strong relationship between pH and schwertmannite saturation in CVL. Schwertmannite was undersaturated in the lake until 2009, when it became oversaturated; 2011 and 2013 results continue this trend (fig. 6.2). For all years before 2009, pH in the lake was below 2.8; pH was above 2.8 from 2009-2013. This
relationship is consistent with the data from Bigham et al (1996) showing the presence of schwertmannite in drainages starting at pH 2.8.

![Schwertmannite saturation in CVL 1997-2013](image)

**Figure 6.6** Schwertmannite saturation model results and pH data in CVL, 1997-2013. Schwertmannite becomes oversaturated in 2009 at a pH of 2.84.

WebPHREEQC inputs for 2013 LRA data from the lake exit, cross-section site, and Salto del Agrio were also input in the excel model to determine schwertmannite saturation in the river itself. At the lake exit, the SI was 4.965, a slight increase from CVL itself. At the bridge, where pH had increased to 3.1, SI was 8.284. At the Salto del Agrio, however, the SI had dropped to -2.707. In the field, the first two sample sites had no ocher on the riverbed, while the Salto del Agrio site was covered in these precipitates. These model results suggest that while the Salto del Agrio site was coated in ocher, in March 2013 schwertmannite was coming out of solution upstream and depleting the Fe,
Al, As and P from the waters. At the upstream sites, schwertmannite may have begun to actively precipitate, though at the time the ocher had not visibly developed on the riverbed. In addition to schwertmannite saturation trends, 2013 LRA WebPHREEQ model results indicated the river was oversaturated in goethite, hematite, and SiO$_2$, as well as jarosite at the lake exit and bridge sample sites. Alunite and gypsum were close to saturation as well.
CHAPTER 7: GEOCHEMICAL RELATIONSHIPS IN THE COPAHUE-CAVIAHUE SYSTEM

This chapter explores the overarching geochemical relationships throughout the Copahue-Caviahue hydrothermal system and seeks to elucidate the geochemical patterns from CP, URA, CVL, and LRA within the context of Copahue’s eruptive activity and hydrothermal output.

The majority of the volcanic contamination of the URA, CVL, and LRA originates at CP. The CP fluids are not fully representative of the “primitive” hydrothermal fluids that undergo W/R interaction in the deep hydrothermal system, as it undergoes further W/R interaction and probably conductive cooling and mixing with meteoric waters in the shallow part of the volcano-hydrothermal system. Earlier studies have documented that the CPL summit crater lake was less neutralized compared to CP and may tap a different section of the underlying hydrothermal reservoir (Ouimette, 2000; Varekamp et al, 2001; 2004; 2009). The absence of the crater lake in 2013 makes any further inferences about that feature with new data not possible.

The degree of W/R interaction can be symbolized with the DON parameter, which is an expression of the percentage of H$^+$ consumed through W/R interaction (Varekamp, 2014). The DON values of the CP and CPL waters are compared for the period 1997 to 2004 (figure 7.1); DON decreases steadily in both types of fluids prior to the 2000 eruption, probably as a result of increased input of magmatic gases prior to the eruption. During the 2000 eruption, the DON parameter increases rapidly, with CP fluids nearly 100% neutralized by 2001. The CPL fluids have still somewhat lower DON values, indicating that the source for CPL inputs may be a more direct line from the hydrothermal reservoir. The higher DON of CP fluids relative to CPL suggests that CP
undergoes more W/R interaction before it surfaces in the spring, which may be related to the permeability structure of the reservoir.

Another signal for the extent of W/R interaction is the atomic ratio of Mg/ΣRFE in CP and CPL fluids. When acid fluids interact with a new protolith, Mg is more readily dissolved from the unaltered rock relative to other RFE (e.g., preferential dissolution of olivine in the largely sulfuric acid). This may lead to a high Mg/ΣRFE during early stages of W/R interaction (Varekamp et al, 2014). Subsequently, Mg/ΣRFE will start to decrease as dissolution of other RFE becomes more prominent and olivine exhaustion occurs. At Copahue, peak Mg/ΣRFE in CPL occurs in 2001, six months after the 2000 eruption (figure 7.2). This value correlates with the initial peak DON for CP and CPL, after which point Mg/ΣRFE in CPL decreases toward pre-eruptive levels. In CP fluids, however, Mg/ΣRFE does not peak until 2002-2003, and DON stays near 100% through this time period. These relationships imply that DON values for CPL had an almost

Figure 7.1 “Degree of neutralization” of Copahue hot springs (CP) fluids and crater lake water, 1997 to 2004. CP fluids become almost 100% neutralized following the 2000 eruption, while crater lake waters have 30% residual acidity even at peak neutralization. “alunite saturation” refers to modeled saturation of alunite in CP fluids following the 2000 eruption (from Varekam, personal communication).
instantaneous response to eruptive activity, while W/R interaction in CP progresses further and at a delayed rate relative to CPL. The effects of these processes are propagated in the VE and RFE concentrations downstream from CP into the URA and CVL.

![Trends in Mg/ΣRFE in Copahue Crater Lake (CPL) and El Vertedero (CP)](image)

**Figure 7.2** Mg/ΣRFE of Copahue crater lake (CPL) and El Vertedero (CP); CPL data from Varekamp et al 2001; 2004; 2009 and Kading, 2010.

The 2012 eruption is associated with similar geochemical trends in Copahue’s hydrothermal geochemistry to the 2000 eruption, with some distinct differences. Over time the concentrations of both VE and RFE in CP fluids has decreased, and URA, CVL and LRA fluids have consequently become more neutralized. As seen in **figure 4.1**, RFE/Cl values in CP increased markedly between 2011 and 2013; CP 2013 RFE/Cl values are significantly higher than in any previous years. While CP fluids showed increased RFE/Cl values following the 2000 eruption (**figure 7.3**), the 2013 increase is unprecedentedly high. RFE/Cl values in 2009 and 2011 were similar to the pre-eruptive 1997-1999 values. While 2000-2001 fluids have higher Mg/Cl and Na/Cl than pre-eruptive years, 2013 fluids are additionally significantly higher in Ca/Cl and Al/Cl.
Figure 7.3 RFE/Cl of CP fluids 1997-2013. Pre-eruptive fluids tend to have lower RFE/Cl (1997, 1999, 2009, 2011), while syn- and post-eruptive fluids have relatively higher RFE/Cl (2000, 2001, 2013). Note strong increase in RFE/Cl following the 2013 eruption.

As the majority of CVL’s VE and RFE come from CP, CVL RFE/Cl values can be expected to evolve toward trends that match CP. CVL is in a constant non-steady-state due to changing fluxes from the URA, dilution in the lake with meteoric water and freshwater tributaries, and outflow of the LRA. As a result, though RFE concentrations in the lake may show positive correlations, it is difficult to parse true compositional responses to CP fluxes from artifacts of non-steady-state dynamics within the lake without extensive numerical modelling (Varekamp, 2008). The RFE/Cl ratios remove some of the noise from these trends, and potential responses to eruptive activity are more apparent. Figure 7.4 shows RFE/Cl for bulk CVL covering the 2000 and 2013 eruptions. More recently (2009-2013) CVL has higher Mg/Cl, Ca/Cl and Na/Cl relative to 1997-2001 values. It is clear that CVL has not yet fully responded to the 2013 spike in RFE/Cl in CP, especially the strong Al/Cl and Ca/Cl enrichment (figure 4.1); unprecedentedly low URA element fluxes following the 2012 eruption compound the
sluggish response time. With its large volume and long residence time (~42 months),
geochemical trends in CVL can be expected to lag CP by several years. Future
monitoring of the Copahue-Caviahue hydrothermal system will likely reveal CVL’s
delayed response to the 2012 eruption.

Figure 7.4 RFE/Cl of CVL waters 1997-2013. Here there is not a significant
pre/post eruptive trend, but we see overall enrichment of Mg, Ca and Na in the 2012
eruptive cycle relative to 2000.

The CP, URA, CVL and LRA each have their own geochemical processes related to
dilution, chemical contributions from tributaries, possibly ongoing W/R interaction in
the river beds and with suspended sediment, mineral saturation and adsorption reactions.
A strong positive correlation is found between Al and K in CP and CVL fluids. A log-
log plot of Al and K concentrations for CP, URA and CVL shows a compelling pattern
(figure 7.5). The Al vs. K values for CP fluids show a moderately strong correlation ($R^2 = 0.68$), while the CVL values correlate very well ($R^2 = 0.82$). As CP is the main source
for Al and K in CVL, the CVL points would be expected to plot along a simple dilution
line. However, the CVL line is offset toward K enrichment but with a parallel slope to the CP line. The URA data form a cloud of intermediate values that extend from the CP line toward the CVL line; the URA 2013 data are especially shifted toward higher K concentrations. A similar log-log plot for Al vs. Fe (figure 7.6) shows a simple linear dilution trend from CP to CVL. This strongly suggests that the URA waters receive a K contribution from tributaries or obtain more K through W/R interaction while flowing through the landscape over 14 km. When plotted together, the whole data set of Al vs. K has $R^2 = 0.896$.

**Figure 7.5 Al vs. K for CP, URA and CVL waters 1997-2013.** CP and CVL show very similar slope trends, but CVL is offset toward lower Al compared to CP. URA values correlate strongly ($R^2 = 0.88$), as do CVL ($R^2 = 0.82$) and CP values ($R^2 = 0.68$). Dotted line shows approximate slope for CVL, solid line shows slope for CP.

In this way the CVL fluids is another window into the effects of the eruption cycles on hydrothermal chemistry. CVL acts as a reservoir for the VE and RFE inputs from the URA; though it is less concentrated, overall trends can be observed that link back to
activity within the hydrothermal system. Care must be taken to define true geochemical relationships in CVL that are related to changes in hydrothermal output, as opposed to compositional fluctuations related to non-steady-state lake dynamics. Overall, geochemical relationships in CVL can be traced back to fluctuations in hydrothermal activity be it with a slight time lag; over time the lake evolves to reflect an amalgamation of past and current fluxes from the URA. Linear geochemical relationships between CVL and CP are quickly lost along the LRA, as rising pH and precipitation of secondary phases skews the relationships between VE and RFE.

Figure 7.6 Al vs. Fe CP, URA, CVL 1997-2013

Figure 7.6 Al vs. K plot for CP, URA, and CVL 1997-2013. Solid line shows approximate slope for all data.
CHAPTER 8: CONCLUSIONS

The geochemistry of surface hydrothermal fluids provides insight into processes within Copahue’s hydrothermal system. New data from 2011 and 2013 fieldwork expand upon previous years’ research of hydrothermal element fluxes in the Copahue-Caviahue system, now including data from two eruption cycles. From 1997 to 2013, concentrations of major and minor volcanogenic (VE) and rock-forming elements (RFE) in El Vertedero hot spring (CP) have fluctuated as a result of geochemical changes within Copahue’s hydrothermal system throughout two eruptive cycles. The compositional trends in CP are passed on to the Upper Río Agrio (URA), Lake Caviahue (CVL), and Lower Río Agrio (LRA); these acid waters continue to evolve as they are transported away from the volcano, via continued precipitation of new phases.

In CP, overall concentrations of VE and RFE have declined from 1997 to 2013; within this general trend we see increased acidity and element export prior to and during the 2000 and 2012 eruptions, with a sharp decline in VE/RFE export immediately following the eruption. Similar geochemical trends in 2004 as well as a “thermal anomaly” in Copahue’s crater lake suggest a small intrusion into the hydrothermal system that did not result in an eruption, but produced similar hydrothermal signatures.

Changes in VE/RFE concentrations in CP over time can be attributed to dilution with meteoric water, incongruent dissolution during W/R interaction, and precipitation of new phases as minerals become saturated in the hydrothermal fluids. CP fluids become more neutralized following an eruption, as indicated by the degree of neutralization of the fluids and increased RFE/Cl values. The decrease in the proportion of magmatic water in the surface hydrothermal fluids following an eruption
indicates decreased fluid mobility from the deep hydrothermal system to the surface. Mineral saturation modeling of CP fluids indicate saturation of alunite and anhydrite in the hydrothermal system just prior to and during eruptions; the precipitation of these minerals in the hydrothermal system likely fills the pore space and reduces the permeability within the system, and thus decreases the output of VE/RFE in surface outlets. The models are corroborated by a strong relationship between Al and K values over time in CP fluids as well as CVL.

Changes in hydrothermal outputs from CP affect the acidity of the URA-CVL-LRA watershed as well as concentrations of VE and RFE. The URA is responsible for the acidification of CVL and import of large quantities of VE and RFE to the lake. CVL acts as a reservoir for VE and RFE, and echoes the signature of URA fluxes for many months. By way of the URA, CVL receives VE and RFE fluxes from tributary streams not associated with CP, altering the relationships between RFE in CVL relative to CP. CVL is saturated in SiO$_2$ and Fe-oxides, and is intermittently saturated with K-jarosite and schwertmannite when pH increases sufficiently. The LRA derives its composition from CVL; RFE and trace contaminants in the LRA are fractionated with the precipitation of schwertmannite on the riverbed; changes in pH affect the location of these precipitates.

Data collected from the 2012 eruption cycle provides new insight to the hydrothermal processes in Copahue. While there are some differences between the 2000 and 2012 eruptive cycles, broad correlations can be drawn regarding the response of CP, URA, CVL and LRA to changes in VE and RFE outputs prior to and after the eruptions.
REFERENCES


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### APPENDICES

**Appendix A: Full 2013 Data Tables**

A.1 (top) Rare earth element (REE) data for 2013 samples. A.2 (bottom) Trace metals of 2013 samples. x – not detected.

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A.1 (top) Rare earth element (REE) data for 2013 samples. A.2 (bottom) Trace metals of 2013 samples. x – not detected.
Appendix B: CVL Depth Profiles

![CVL CI by depth 2013](image1)

![CVL SO4 by depth 2013](image2)