New insight from noble gas and stable isotopes of geothermal/hydrothermal fluids at Caviahue-Copahue Volcanic Complex: Boiling steam separation and water-rock interaction at shallow depth

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We measured noble gas and stable isotopes of the geothermal and hydrothermal fluids of the Caviahue-Copahue Volcanic Complex (CCVC), one of the most important geothermal systems in Argentina/Chile, in order to provide new insights into fluid circulation and origin. With the exception of Anfiteatro and Chango-co geothermal systems, mantle-derived helium dominates in the CCVC fluids, with measured $^3\text{He}/^4\text{He}$ ratios up to 7.86Ra in 2015. Their positive $\delta^{15}\text{N}$ is an evidence for subducted sediment-derived nitrogen, which is commonly observed in subduction settings. Both He-N2-Ar composition and positive correlation between $\delta^{18}\text{O}$-H2O and $\delta^{13}$C suggest the fluids from Anfiteatro and Chango-co (and partly from Pucón-Mahuida as well, on the southern flank of Copahue volcano) represent a meteoric water composition with a minor magmatic contribution. The Ne, Kr and Xe isotopic compositions are entirely of atmospheric origin, but processes of boiling and steam separation have led to fractionation of their elemental abundances. We modeled the CCVC fluid evolution using Rayleigh distillation curves, considering an initial air saturated geothermal water (ASGW) end-member at 250 and 300 °C, followed by boiling and steam separation at lower temperatures (from 200 °C to 150 °C). Between 2014 and 2015, the CCVC hydrogen and oxygen isotopes shifted from local meteoric water-dominated to andesitic water-dominated signature. This shift is associated with an increase of $\delta^{13}$C values and $S_{\text{total}}$, HCl and He contents. These characteristics are consistent with a change in the gas ascent pathway between 2014 and 2015, which in turn induced higher magmatic-hydrothermal contribution in the fluid signature. The composition of the magmatic source of the CCVC fluids is: $^3\text{He}/^4\text{He} = 7.78a$, $\delta^{15}\text{N} = +6.5\%$, and $\delta^{13}$C = $-6.5\%$. Mixing models between air-corrected He and N suggest the involvement of 0.5% to 5% of subducted sediments in the magmatic source. The magmatic sulfur isotopic composition is estimated at $-2.38\%$ (from COP-2), but most samples show elemental fractionation due to boiling and steam separation followed by various degrees of atmospheric contamination. All these geochemical and isotopic characteristics are the direct consequence of tectonic particularities of the CCVC: NE faults promote the ascent of hydrothermal fluids in the geothermal area whereas WNW faults serve as preferential channels for meteoric water infiltration.

1. Introduction

Noble gases have great potential as tracers for mantle sources and fingerprinting of geothermal reservoirs (Sano and Fischer, 2013; Pinti et al., 2013). The noble gases present in hydrothermal fluids are from three potential sources: the crust, the mantle, and the atmosphere. Hydrothermal fluids are characterized by freshwater that contains atmospheric noble gases dissolved during recharge. This water in a geothermal reservoir is responsible for continuous energy and mass transfer from depth to the surface. Over time, this water geochemically evolves due to addition of radiogenic isotopes ($^4\text{He}$ and $^{40}\text{Ar}$) during continuous high-temperature water-rock interactions (Kennedy and van Soest, 2006). Most importantly, the He isotopic composition differs by three orders of magnitude between crust and mantle. Thus, this value has the potential to distinguish He mantle-derived fluids that provide the heat energy from the magmatic activity into the system (Sano and Fischer, 2013; Hilton et al., 2002). The implication of the three above-mentioned components in the geothermal system is essential to understand the origin of the thermal fluids, their pathway and subsurface interaction. Noble gases have a low solubility in freshwater, particularly at
high temperature (Crovetto et al., 1982). Phase separation during boiling in the geothermal system can generate a residual liquid that becomes depleted in noble gases and isotopically fractionated compared to the initial fluid composition. Thus, noble gases are useful to discriminate the magmatic origin, constrain active geothermal areas of interest, and determine physical processes related to magmatic degassing or hydrothermal circulation. Therefore, we performed a study of noble gases along with stable isotopes at the Caviahue-Copahue Volcanic Complex (CCVC) where magma emplacement and fluid flow are strongly controlled by the northern termination of the Liquiñe-Ofqui Fault Zone (LOFZ) associated with a second-order anisotropy of overall NE-SW and NW-SE orientation. This geothermal/hydrothermal system of CCVC has been investigated for various purposes; geothermic energy and volcanic risk. However, some lacks still exist about the processes of boiling and steam separation and the location of the water recharge area. Previous study from Agusto et al. (2013) suggests the presence of preferential water recharge of the geothermal system in Chancho-co and Anfiteatro areas, additionally with the water recharge coming from the flank of the Copahue volcano. Agusto and Varekamp (2015) indicated that the evaporation process occurs in the geothermal system at the same temperature (30 °C) that as the Copahue crater lake (30 °C represents the low-end range temperature of the crater lake). Knowing that the geothermal reservoir has a temperature of 250 °C–300 °C (Agusto et al., 2013) and that the temperature of fumaroles and bubbling gas is around the boiling temperature, it is difficult to confirm an evaporation process at 30 °C.

Thus, in the present study, we present new chemical and isotopic composition ($\delta^{15}$N, $\delta^{13}$C-CO$_2$, $\delta^{13}$C-CH$_4$, $\delta^{34}$S, He/He, $\delta^{18}$O-H$_2$O, and $\delta^{18}$O-H$_2$O) of fumaroles, bubbling gases from thermal springs, and one well surrounding the CCVC, all collected in 2014 and 2015, that explore the possibility that Chancho-co and Anfiteatro represent preferential areas of fluid-rock-groundwater interaction without any implication for water recharge of the geothermal system. We also suggest that the boiling steam separation is effective between 190 °C and 150 °C that corresponds more or less at the temperature of the vapor-dominated zone (180 °C–200 °C; Agusto et al., 2013). Thus, the aim of this work is to couple noble gases with other water tracers in order to: 1) better identify water-rock-fluid interactions at shallow depth, 2) determine how boiling and steam separation affect the elemental and isotopic fractionation, 3) identify the deep magmatic source, and 4) establish a relationship between the geochemical composition of the geothermal fluids and the fault network.

2. Geology

In the Southern Volcanic Zone (SVZ) of Chile and Argentina, geothermal activity occurs in close spatial relationship with active volcanism along the Cordillera which is primarily controlled by the ~1000 km long, NNE-trending Liquiñe-Ofqui Fault Zone (LOFZ), an intra-arc dextral strike-slip fault system associated with second-order anisotropy of overall NE-SW (extensional) and NW-SE (compressional) orientation (Fig. 1) (Cembrano et al., 1992, 1996, 2000; Cembrano and Lara, 2009).

The Caviahue-Copahue Volcanic Complex (CCVC) is located at 37.5°S, 71°W, at the border between Argentina and Chile (Fig. 1), and is composed of the Caviahue caldera and the Copahue stratovolcano (Fig. 1). Structurally, the CCVC is located in the accommodation zone at the northern termination of the LOFZ (Melnick et al., 2006). The Caviahue caldera is a square-shaped depression of ca. 20 km × 15 km, defined as a transitional pull-apart, intra-arc basin due to the local stress field generated by the interaction of the LOFZ and the Antihir Copahue.
fault zone (ACFZ). The ACFZ is a thrust system that begins at the latitude of the Caviahue caldera and is responsible for its development.

The history of the Caviahue caldera started at 3–4 Ma with the opening of a pull-apart caldera. The walls and basement of the Caviahue caldera are defined by the Cola de Zorro Formation (5–6 Ma; Linares et al., 1999), which is composed of basaltic and andesitic lavas, volcanic breccias and minor sedimentary beds continuously exposed in the main Cordillera between 36° and 39°S. Las Mellizas volcano formed inside the caldera is composed of three sequences: lower lavas, ignimbrites, and upper lavas. The ignimbrites represent the collapse of Las Mellizas stratovolcano (Melnick et al., 2006) dated by K/Ar at 3.2 ± 0.14 Ma and 2.6 ± 0.1 Ma (Linares et al., 1999). The Copahue volcano is an active adesitic to basaltic–andesitic stratovolcano nested on the western rim of the Caviahue caldera. Volcanic activity at Copahue began at approximately 1 Ma ago. However, since the Upper Pleistocene and postglacial period, activity has consisted mainly in effusive emissions of andesitic lava flows and only a few explosive episodes during the Holocene that generated at least 6 ash flows (Linares et al., 1999; Muñoz and Stern, 1988). During the last 250 years, the Copahue eruptions have consisted in weak phreatic and phreatomagmatic events. Since Nov.–Dec. 2011, the discharge of fluids from the summit of Copahue volcano has significantly increased and intermittent phreatic events occurred since 2012, with a big eruption reported in Dec. 2012 (Caselli et al., 2015). Copahue volcano holds an acidic crater lake (Temp.: 8 °C–19 °C; pH ~ 0.2–1.1; Varekamp et al., 2009; Agusto and Varekamp, 2015: Fig. 1) and acidic hot springs called Vertientes (V; Temp.: 40 °C–70 °C; pH ~ 0.3–2.4; Fig. 1) near the summit area; all feed the Agrio river (pH ~ 0.5–2.5). This river discharges into a large glacial lake, called Lake Caviahue, and acidificid it (pH: 2.1–2.7; Agusto, 2011; Caselli et al., 2005; Varekamp et al., 2001, 2006).

Five geothermal areas are recognized in the region, with surface manifestations including boiling pools and bubbling pools with temperatures reaching up to 96 °C, and fumaroles that reach temperatures of up to 135 °C (Agusto et al., 2007). The Las Maquinas (LM), Las Maquinitas (LMM), Termas de Copahue (TC-LV), Cabanita (CB) and Anfiteatro (AF) thermal areas are located northeast of the volcano and appear to be controlled by the northeast structures (Melnick et al., 2006). The Chancho-co (CC) geothermal field is located on the northern flank of the volcano, in close proximity to the volcanic–hydrothermal system (Velez et al., 2011). The Pucón-Mahuida (PM) bubbling gas manifestation lies in the southern flank of Copahue volcano and represents a direct manifestation of the hydrothermal system from Copahue volcano (Fig. 1). The geothermal field of CCVC had been defined as a vapor-dominated field with stratified layers connected by fractures with increased vertical permeability within the reservoir (Agusto et al., 2013; Panarello, 2002; JICA, 1992). During geothermal exploration of the CCVC, a vapor-dominated hydrothermal system was recognized in its northeastern part, composed of two different productive reservoirs located at depths of 800–1000 m and 1400 m, with temperatures estimated from geothermometry at 180–200 °C and 250–300 °C, respectively (Agusto et al., 2013), whereas the basis of temperature from drilling ranges from 235 °C (COP-2 and COP-4) to 250 °C (COP-1; Mas and Mas, 2015). According to the measurements carried out in the wells drilled up to now, the reservoir parameters were defined by a static pressure up to 4 MPa and a flow rate up to 50–60 t/h (Mas, 2005).

### 3. Sampling and methods

During 2014 and 2015, we collected twenty gas samples, more duplicate, from fumaroles, bubbling gases, one water and one well (COP-2), all from the CCVC geothermal areas. Fumarole gases were sampled using a titanium tube connected by a silicone tube to an alkaline glass bottle and cold trap. The alkaline glass bottle and cold trap were plunged in cold water. Bubbling gas samples were collected using an alkaline glass container with vacuum valves at both ends, following a water displacement method. Gas samples from fumarole and bubbling gas emanation were also collected into Pyrex flasks (Giggenbach bottles) containing 20 mL of 4 N NaOH solution for absorption of acid gas for gas composition analyses. One water sample from the natural hot spring from Chancho-co was collected in alkaline glass containers using a manual pump.

Noble gases were analyzed at the Noble Gas Laboratory of the University of Michigan, USA. Gas samples were attached to a vacuum extraction system and noble gases were quantitatively extracted for infilling into a MAP-215 mass spectrometer for isotopic analyses. Extracted gases were passed over a Ti sponge getter to remove reactive gases from the samples.

### Table 1: Chemical composition of the dry gas fraction (in ppm) and water vapor (in %) of the CCVC gases.

<table>
<thead>
<tr>
<th>Location of analyzes</th>
<th>Sample Type</th>
<th>Date</th>
<th>CO₂</th>
<th>N₂</th>
<th>CH₄</th>
<th>H₂</th>
<th>HCl</th>
<th>HF</th>
<th>Ar</th>
<th>O₂</th>
<th>He</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taiwan</td>
<td>COP-LM-FI-14</td>
<td>2014</td>
<td>944354</td>
<td>10187</td>
<td>18813</td>
<td>10930</td>
<td>15485</td>
<td>203</td>
<td>n.d.</td>
<td>n.d.</td>
<td>9.64</td>
<td>97.58</td>
</tr>
<tr>
<td>Taiwan</td>
<td>COP-LM-FI-14</td>
<td>2014</td>
<td>941690</td>
<td>7390</td>
<td>15450</td>
<td>17380</td>
<td>17804</td>
<td>261</td>
<td>n.d.</td>
<td>n.d.</td>
<td>6.02</td>
<td>97.53</td>
</tr>
<tr>
<td>Taiwan</td>
<td>COP-CF-FI-14</td>
<td>2014</td>
<td>884104</td>
<td>81640</td>
<td>995</td>
<td>740</td>
<td>27342</td>
<td>663</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.36</td>
<td>99.25</td>
</tr>
<tr>
<td>Taiwan</td>
<td>COP-LM-BG-14</td>
<td>2014</td>
<td>921650</td>
<td>12110</td>
<td>28397</td>
<td>15385</td>
<td>22044</td>
<td>313</td>
<td>n.d.</td>
<td>n.d.</td>
<td>56.81</td>
<td>15.82</td>
</tr>
<tr>
<td>Taiwan</td>
<td>COP-CB-FI-14</td>
<td>2014</td>
<td>941371</td>
<td>17378</td>
<td>28856</td>
<td>10045</td>
<td>2006</td>
<td>372</td>
<td>n.d.</td>
<td>n.d.</td>
<td>6.02</td>
<td>97.53</td>
</tr>
<tr>
<td>Taiwan</td>
<td>COP-CB-GW-15</td>
<td>2015</td>
<td>925573</td>
<td>18342</td>
<td>29477</td>
<td>17484</td>
<td>11366</td>
<td>491</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.36</td>
<td>99.25</td>
</tr>
<tr>
<td>Taiwan</td>
<td>COP-AF-FI-15</td>
<td>2015</td>
<td>826200</td>
<td>90696</td>
<td>54300</td>
<td>44408</td>
<td>14553</td>
<td>592</td>
<td>815</td>
<td>19.6</td>
<td>43.61</td>
<td>98.78</td>
</tr>
<tr>
<td>China</td>
<td>COP-PB-15</td>
<td>2015</td>
<td>970450</td>
<td>18523</td>
<td>8170</td>
<td>201</td>
<td>n.d.</td>
<td>268</td>
<td>66</td>
<td>146</td>
<td>1583</td>
<td>3.32</td>
</tr>
<tr>
<td>Taiwan</td>
<td>COP-LM-FI-15</td>
<td>2015</td>
<td>905588</td>
<td>27735</td>
<td>31479</td>
<td>20653</td>
<td>13535</td>
<td>647</td>
<td>229</td>
<td>61</td>
<td>43.87</td>
<td>14.02</td>
</tr>
<tr>
<td>Taiwan</td>
<td>COP-CF-FI-15</td>
<td>2015</td>
<td>652434</td>
<td>261853</td>
<td>19715</td>
<td>3823</td>
<td>50577</td>
<td>6249</td>
<td>4606</td>
<td>273</td>
<td>473</td>
<td>16.66</td>
</tr>
<tr>
<td>Taiwan</td>
<td>COP-CB-FI-15</td>
<td>2015</td>
<td>912957</td>
<td>28095</td>
<td>28981</td>
<td>14897</td>
<td>9163</td>
<td>792</td>
<td>62</td>
<td>8.4</td>
<td>12.03</td>
<td>97.52</td>
</tr>
</tbody>
</table>

Note: Stotal is mainly composed of H₂S. n.d.: not detected.
The CO2/3He and CH4/3He ratios were calculated using 3He/4He and CO2/He, and CH4/He, respectively. (a) Data from Tardani et al. (2016). (b) Percentage of experimental errors were estimated to be about ± 10% by repeated measurements of standard samples. The measured blank for each component was negligibly small.

Note: n.a.: not analyzed. *: Gas composition was determined by comparing peak heights of the samples with those of standard gases, using a quadrupole mass spectrometer at AORI-The University of Tokyo.

δ15N, δ34S, δ13C-CO2 and δ13C-CH4 are less than ±0.2‰, ±0.3‰, ±0.2‰, and ±0.3‰, respectively. It is relevant to note that the δ34S values refer to the composition of total sulfur that is mainly composed of H2S.

Oxygen and hydrogen isotopic compositions were determined using an ISOpal stable isotope ratio mass spectrometer at GEOTOP-UQAM (Canada). Measurement uncertainty for 18O and 2H is ±0.5‰ (1 s) and ±1‰ (1 s), respectively.

Gas compositions in fluids were determined at the University of New Mexico, USA, for samples collected in 2015. Inert gases (N2, O2, H2, He, Ar, and CO) were analyzed on a Pfeiffer Quadrupole Mass Spectrometer (QMS). Calibration of the QMS was performed with standard gas mixtures (Scott Specialty Gases; de Moor et al., 2013a). The QMS analyses have a precision of <0.1% (concentration). Carbon dioxide concentrations were determined by titration of NaOH solutions using 0.1 N HCl. Total S was determined gravimetrically after precipitation of BaSO4 from the NaOH solutions, and SO2/H2S was measured by alkaline iodine titration (Giggenbach and Goguel, 1989).

For samples collected in 2014, gas compositions were determined at the National Taiwan University, Taiwan. Inert gases were analyzed by a gas chromatograph (GC, SRI 8610C). HCl and total sulfur were analyzed with an ion chromatograph (IC, Metrohm 790 Personal). The titration method was applied to measure the CO2 concentration, (Metrohm 702 SM Titatron) by assuming that all of the CO2 inside the sample had been dissolved as CO32-. The SO2/H2S proportion was measured by alkaline iodine titration (Lee et al., 2005).

4. Results
4.1. Chemical composition of the CCVC fluids

We report in Table 1 the chemical composition of the dry gas fraction and the molar percentage of water vapor for the CCVC fluids, sampled in 2014 and 2015. The water vapor proportion in fumaroles, bubbling gases and a geothermal well from the CCVC is higher than 95%. The dry gas phase from the CCVC fluids is dominated by CO2, with around 920,000 ppm for Las Maquinas (LM), Las Maquinitas (LMM), Cabalita (CB), COP-2 (C2), and Pucon-Mahuida (PM), whereas it is lower in ...
fluids from Chancho-co (CC) and Anfiteatro (AF) (652,434 ppm to 826,200 ppm). Relatively high concentrations of total S (mainly H2S; from 7390 to 26,1853 ppm), N2 (from 995 to 550 ppm) and CH4 (from 201 to 44,408 ppm) are observed. The acidic gas species HCl and HF are detected in some samples, ranging from 172 to 6249 ppm and from 66 to 4606 ppm, respectively. The Ar and He concentration is up to 814 ppm and 43 ppm, respectively. In a He-Ar-N ternary diagram (Fig. 2), the CCVC fluids are defined as having an andesitic composition similar to that of subduction zone gases. However, three samples (namely, PM, AF and CC) also present a combination of Air-Saturated Water (ASW) and/or an air component.

4.2. Isotopic composition of gases (δ15N, δ13C-CO₂, δ13C-CH₄, δ18S) and water vapor (δD-H₂O, δ18O-H₂O)

The values of δD-H₂O and δ18O-H₂O in condensate samples vary over time (Table 2). In 2014 and 2015, δD-H₂O ranged from −109.3‰ to −85.5‰ and from −89.6‰ to −47.8‰, respectively, whereas δ18O-H₂O varied between −18.25‰ and −10.65‰ in 2014, and between −12.11‰ and 0.92‰ in 2015.

The δ15N values of all CCVC fluids ranged from 0.77‰ to 4.93‰ (Table 2).

The δ13C-CO₂ values for fumaroles and bubbling gases in 2014 ranged from −7.38‰ to −98.2‰, but varied from −6.02‰ to −6.92‰ in 2015 (Table 2). The only water sample from Chancho-co (CC; collected in 2015) had a δ13C-CO₂ value of −8.24‰. With δ13C-CO₂ of −11.87‰ in 2014 and −10.42‰ in 2015, the samples from Pucon-Mahuida (PM) show a significantly lower value than that of all the geothermal areas.

The δ13C-CH₄ of all CCVC fluids excluding Chancho-co (CC) and Anfiteatro (AF) ranged from −34.38‰ to −30.77‰ in 2014 and from −30.16‰ to −18.23‰ in 2015 (Table 2). The δ13C-CH₄ value from AF was −45.99‰ in 2014 and ranges from −37.51‰ to −30.81‰ in 2015. The δ13C-CH₄ value from CC was −36.36‰ in 2015.

The δ15S values from CCVC fluids show a large variation, from −4.86‰ to 2.56‰.

4.3. Noble gas isotopes

The 3He/4He ratios (R/Ra) of Las Maquinas (LM), Las Maquinitas (LMM), Termas Copahue (TC-LV), and Cabahita (CB) samples varied between 7.09Ra and 7.86Ra (Table 2). Values for Chancho-co (CC) and Anfiteatro (AF) ranged from 3.65Ra to 5.37Ra, and from 6.16Ra to 6.49Ra for Pucon-Mahuida (PM). Fig. 3 illustrates the variation of R/Ra in the CCVC fluids against the He/3He ratios. The regression curve suggests that He isotopic composition of the CCVC fluids results from the mixing between air (ASW; 1Ra) and a mantle component estimated at 7.7Ra. The samples from Pucon-Mahuida, Chancho-co and Anfiteatro represent a mixing between ASW (1Ra) and values of 6.4Ra and 5.3Ra, respectively, suggesting addition of radiogenic 4He in the hydrothermal system from shallow environment (meteoric water and/or local sediments).

The 20Ne/22Ne and 21Ne/22Ne isotopic ratios of the CCVC fluids ranged from 9.54 to 10.22 and from 0.0269 to 0.0292, respectively (Appendix A). The 129Xe/130Xe and 136Xe/130Xe isotopic ratios also vary within the range of normal mantle values.
showed low variation, from 6.294 to 6.523 and from 2.171 to 2.180, respectively (Appendix A). These values are totally similar to the atmospheric component (9.80, 0.0290, 6.496 and 2.176, respectively; Ozima and Podosek, 2002), but they might account for a slight mass fractionation by gaseous diffusion too (Marty, 1984). The 38Ar/36Ar isotope ratios were also atmospheric (0.188; Appendix A). In contrast, the 40Ar/36Ar ratios (287.5 to 371.2; Table 2) were similar or higher than that of the atmosphere component (295.5; Ozima and Podosek, 2002), suggesting that they reflect the source of the CCVC fluids.

5. Discussion

5.1. Boiling-steam separation and meteoric water recharge: evidence of elemental fractionation of noble gases

Neon and xenon isotopes have great potential as tracers for mantle sources and fingerprinting of geothermal reservoirs. 36Ne/32Ne and 21Ne/32Ne ratios are high in MORB (12.6 and 0.060, respectively) compared to air (9.8 and 0.0290, respectively; Moreira and Kurz, 2013), while hydrothermal fluids from different settings are characterized by significant air contribution or highly fractionation-related 20Ne/21Ne values. In Iceland and Yellowstone (USA), Ne isotopes show mixing between a MORB-type mantle and air components (Sano and Fischer, 2013, and authors therein). However, in subduction settings, 20Ne/36Ne and 21Ne/32Ne ratios suggest a significant crustal contribution (Tedesco et al., 1998), with the exception of Etna volcano that has extremely high 20Ne/21Ne and 21Ne/32Ne ratios, close to the MORB field (Nakai et al., 1997). Xenon has many isotopes but the most representative ratios are 129Xe/130Xe and 136Xe/130Xe. The MORB 129Xe/130Xe and 136Xe/130Xe ratios lie at 7.7 (Moreira and Kurz, 2013) and 2.6 (Trieloff et al., 2000), respectively. In subduction settings, xenon from hydrothermal fluids mainly originates from the atmosphere (129Xe/130Xe = 6.49 and 136Xe/130Xe = 2.16; Pinti et al., 2013).

The Ne and Xe (and Kr) isotope ratios of the CCVC fluids are close to atmospheric values (Appendix A) and show a slight mass fractionation by gaseous diffusion (Marty, 1984). These two observations represent typical isotopic characteristics in arc setting but cannot help the better understanding of the CCVC fluid features because the original Ne, Xe and Kr isotopic compositions are masked by these two processes.

Noble gas relative abundances (Table 3) are given using the F-value notation (Ozima and Podosek, 2002) in which measured abundances are normalized to the air abundance with 36Ar as the reference isotope [e.g., F(i) = (i / 36Ar)sample / (i / 36Ar)air]. Pinti et al. (2013) presented F(132Xe), F(20Ne) and F(84Kr) data from Los Azufres (Mexico) and showed that elemental abundances can be useful fingerprints of physical changes in the reservoir caused by boiling and steam separation and meteoric water interaction, and are easily fractionated compared to the equilibrium solubility concentrations (Mazor and Truesdell, 1984). Fig. 4A shows F(132Xe) versus R/Ra values measured in the CCVC fluids in 2014 (black circle) and 2015 (empty circle). R/Ra and F(i) values for the atmosphere (Air), Air-Saturated Water (ASW) at 5 °C, and Air-Saturated Geothermal Water (ASGW) at a reservoir temperature of 250–300 °C (CO2–CH4 production; Agusto et al., 2013) are also reported.
(Crocketto et al., 1982; Ozima and Podosek, 2002). Most of CCVC fluid samples display a constant $R/R_a$ ($\approx 7.5Ra$) with the increase of $F(^{132}Xe)$, departing from the expected ASGW composition. This could be explained by fractionation of noble gases due to boiling and steam separation. However, $R/R_a$ and $F(^{132}Xe)$ for Pucón-Mahuida (PM), Anfiteatro (AF), and Chancho-co (CC) gradually decrease from the Cabalgata (CB) values. This, in conjunction with what was previously stated based on the He-$N_2$-Ar ternary diagram (Fig. 2) about these three locations (i.e. PM, AF, and CC show a mixing with ASW and/or air components), supports the conclusion that PM, AF, and CC may be the result of massive ASW and air addition from meteoric water probably related to the interaction with groundwater at shallow depth. Finally, this Fig. 4A indicates that samples 2015 LMM, 2015 TC and 2014 CB, plotted close to ASGW (geothermal compositional field), represent the initial isotopic composition of geothermal system.

Fig. 4B displays $F(^{132}Xe)$ versus $F(^{84}Kr)$ values in the CCVC fluids. Most samples start from ASGW elemental compositions and are explained by two processes: 1) boiling and steam separation at hydrothermal reservoir depth and 2) mixing with meteoric water and/or air (probably at shallow depth). During boiling and steam separation, more soluble heavier noble gases ($Kr$ and $Xe$ compared to $Ar$) are retained in the residual liquid. This process of elemental fractionation can be modeled as a Rayleigh distillation process, if we assume that the vapor phase is continuously removed from the system. In residual liquid, this process is given by the following equation (Ma, 2009):

$$i \frac{^{36}Ar}{C_0}/C_1 = f \left( i \frac{^{36}Ar}{k^{36}Ar} - 1 \right)$$

where $i^{36}Ar$ is the fraction of $^{36}Ar$ remaining in the residual liquid following boiling and steam separation and $k$ is the solubility value (Crocketto et al., 1982; Ozima and Podosek, 2002).

In Fig. 4B, the pink and purple curves are simulated considering an initial ASGW of 250 (purple diamond) and 300 °C (pink diamond) followed by boiling and steam separation at lower temperature, from 200 °C to 150 °C. These simulations reproduce the elemental fractionation pattern observed in the CCVC fluids. Most $F(^{132}Xe)$ and $F(^{84}Kr)$ data for the CCVC fluids plot close to the simulated fractionation curves for a residual liquid after steam separation (Fig. 4B) or close to ASGW (pink and purple diamonds), with the exception of the CC sample collected in 2014 that plots at slightly lower $F(^{84}Kr)$. This 2014-CC sample can be explained by a second process of elemental fractionation compatible with a separated steam phase, as observed in Los Azufres fluids (Mexico; Pinti et al., 2013). Alternatively, this 2014-CC value may also reflect a strong level of atmospheric contamination as observed in Fig. 4A.

In summary, with the exception of 2015-TC, 2014-CC, and 2015-LMM, all samples show strong elemental fractionation of noble gases due to boiling and steam separation in the hydrothermal reservoir, providing fluids to the geothermal fields of CCVC. Anfiteatro (AF), located at the northwestern part of CCVC, and Chancho-co, located at the northern flank of Copahue are strongly contaminated by air related to the involvement of meteoric water probably from shallow aquifer (fluid-rock-water interaction). This is consistent with the hypothesis presented in Roullée et al. (2015) that Anfiteatro lies outside the high vapor zone which facilitates the direct ascent of hydrothermal fluids to the surface. Pucón-Mahuida (PM) is also significantly contaminated by air. This hydrothermal area is located in the southern flank of Copahue volcano and could be defined as a particular water recharge area as it was proposed that the flank of Copahue is a preferential zone for water recharge (Agusto et al., 2013; Velez et al., 2011).

5.2. δD-H2O, δ18O-H2O δ13C signature in CCVC fluids

The water isotopes could be investigated to determine the origin of the hydrothermal fluids and also to characterize chemical and physical processes such as water-rock interaction and boiling processes (evaporation).

Fig. 5 presents the δD-H2O versus δ18O-H2O plot, where the Global Meteoric Water Line (GMWL; Craig, 1961), andesitic water (Giggenbach, 1992) and magmatic water (Sheppard and Epstein, 1970) are reported. Vertientes and Crater lake data are from Agusto and Varekamp (2015). Evaporation line is defined from the calculation reported in Varekamp and Kreulen (2000). Andesitic water is defined as the isotopic composition of recycled seawater coming from the subduction zone. Magmatic water represents the isotopic composition of water in equilibrium with an unaltered magmatic body.

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processes 1) magmatic contribution, consequently higher magmatic input in the CCVC geothermal system (consistent with the Vertiente composition) and 2) evaporation process as it is proposed for the water isotopic composition of Copahue crater lake. At this step, it is difficult to prove one or another hypothesis. To confirm one of these hypotheses, we compared the water and carbon isotope evolution between 2014 and 2015.

Fig. 6 presents $\delta^{13}$C-$\text{CO}_2$ values against $\text{CO}_2/\text{He}$ ratios from the CCVC fluids. Typical $\text{CO}_2/\text{He}$ and $\delta^{13}$C-$\text{CO}_2$ values for MORBs are $2 \times 10^6$ and $-6.5 \pm 2.5\%$o, respectively (Sano and Marty, 1995; Sano and Williams, 1996). The $\text{CO}_2/\text{He}$ ratio for the crust ranges from $1 \times 10^{12}$ to $1 \times 10^{14}$, whereas its $\delta^{13}$C-$\text{CO}_2$ composition varies between two major components (Hoefs, 2009): (1) organic sediments (−40% to −20%), and (2) marine limestone (including slab carbonates) (0 ± 2%). For comparison, the volcanic arc average values for $\text{CO}_2/\text{He}$ and $\delta^{13}$C-$\text{CO}_2$ are $1.5 \pm 1.1 \times 10^{10}$ (Sano and Williams, 1996) and −5.5 ± 2.2%o (Sano and Marty, 1995), respectively.

The mixing curve follows:

$$\delta^{13}\text{C}_{\text{obs}} = \text{Lim} \cdot \delta^{13}\text{C}_{\text{Lim}} + \text{MORB} \cdot \delta^{13}\text{C}_{\text{MORB}} + \text{Sed} \cdot \delta^{13}\text{C}_{\text{Sed}} \quad (3)$$

$$1/(\text{CO}_2/\text{He})_{\text{obs}} = \text{Lim}/(\text{CO}_2/\text{He}_{\text{Lim}}) + \text{MORB}/(\text{CO}_2/\text{He}_{\text{MORB}}) + \text{Sed}/(\text{CO}_2/\text{He}_{\text{Sed}}) \quad (4)$$

$$\text{MORB} \cdot \text{Sed} + \text{Lim} = 1 \quad (5)$$

where obs, Lim, Morb, and Sed refer to: the observed value, Limestone, MORB, and sediments, respectively.

The carbon contribution of the CCVC gases is as follows: 56–74% limestone, 16–34% organic sediments, and 2–30% MORB (Table 2). However, we note a significant difference of $\text{CO}_2/\text{He}$ and $\delta^{13}$C-$\text{CO}_2$ for samples collected in 2014 versus 2015. Our samples collected in 2014 present similar carbon compositions as for the samples collected in 2012 by Agusto et al. (2013). In contrast, our samples collected in 2015 display lower $\text{CO}_2/\text{He}$ and $\delta^{13}$C-$\text{CO}_2$ values compared to the ones for 2006–2007 and 2012 (Agusto et al., 2013), and 2014. The average $\delta^{13}$C-$\text{CO}_2$ and $\text{CO}_2/\text{He}$ compositions for the 2014 CCVC gas samples (excluding PM and CC samples that depart from the main cluster of points) are −7.84‰ and 12.1×10^9, respectively. The 2015 CCVC fluids average changes to −6.5‰ and 6.4×10^9, respectively (excluding PM and CC). For the two field campaigns, LMM appears as the most primitive sample, with the lowest $\delta^{13}$C-$\text{CO}_2$ and $\text{CO}_2/\text{He}$: −7.38‰ and 5.5×10^9, respectively for 2014, and −6.02‰ and 4.67×10^9, respectively for 2015 (Fig. 6). The decrease of $\text{CO}_2/\text{He}$ and the increase of $\delta^{13}$C-$\text{CO}_2$ in our samples from 2014 to 2015 suggest a significant change in the chemistry of the CCVC fluids. The CC and PM samples present both the lowest $\delta^{13}$C-$\text{CO}_2$ values and the highest $\text{CO}_2/\text{He}$ ratios. This is an evidence for significant contamination by local sediments (organic sediments; Fig. 6).

There are two possible explanations for the observed isotopic and chemical variations: (1) a change in the sources and (2) a modification in the path for gas ascent. The gas compositions presented in this study reveal an increase trend between 2014 and 2015, mainly in the $S_{\text{total}}$, HCl and He contents (Table 1). However, no significant increase of R/Ra is observed, hence no new magmatic signature is detected. Furthermore, these changes are also associated with a combined increase of $\delta^{13}$C-$\text{CH}_4$ (from −34.4‰ in 2014 to −28.07‰ in 2015, LM sample, Table 2), $\delta D$-$\text{H}_2\text{O}$ and $\delta^{18}$O-$\text{H}_2\text{O}$, suggesting a decrease of (meteoric) water-rock interaction in the hydrothermal system and a probable increase of the magmatic input. The same compositional and isotopic evolution is observed at Tatun volcano, Taiwan (Lan et al., 2007; Roulleau et al., 2015b). Based on unmodified He isotopic ratios, Lan et al. (2007) proposed that the carbon isotopic variation is the result of a modification in the path of gas ascent. Roulleau et al. (2015a) proposed that the variation of carbon composition over time is the result of variable amount of sediments versus limestone incorporation in the subduction zone, and/or variation of crustal contamination from local sediments. Thus, it is reasonable to argue for a higher magmatic input related to the modification of the gas ascent path that may generate in turn a decrease of local sediments contamination. This hypothesis needs to be confirmed through further monitoring in the field.

5.3. Origin of $\text{He}$ and $\text{N}$ in the CCVC fluids: interplay between MORB and sediments

The potential gas source of the CCVC fluids can be investigated by using $\text{N}_2$/He against $\delta^{15}$N (Fig. 7; Fischer et al., 2002), where the nitrogen composition is represented by a mixing line between three
and sediments, respectively. All calculations are presented in Table 2.

where \( \delta^{15}N_{\text{obs}} \), Air, Morb, and Sed refer to: the observed value, Air, Morb, and COP-2 (Chancho-co and An) have expected to result in higher N2/He ratios and with the incorporation of air and/or sediment-derived nitrogen to the mantle source is consistent with the published range for arc-related volcanoes (de Moor et al., 2013a; Fischer et al., 2002; Roulleau et al., 2013, 2015b; Sano et al., 2001). The mixing curve follows:

\[
\delta^{15}N_{\text{obs}} = \text{Air} \delta^{15}N_{\text{Air}} + \text{Morb} \delta^{15}N_{\text{MORB}} + \text{Sed} \delta^{15}N_{\text{Sed}}
\]

\[
1/(N_2/He)_{\text{obs}} = (N_2/He_{\text{Air}})/(\text{Air}) + (N_2/He_{\text{MORB}})/(\text{Morb}) + (N_2/He_{\text{Sed}})/(\text{Sed})
\]

\[
\text{Morb} + \text{Sed} + \text{Air} = 1
\]

where obs, Air, Morb, and Sed refer to: the observed value, Air, Morb, and sediments, respectively. All calculations are presented in Table 2.

The mixing model of subducted sulfate and sedimentary pyrite (Kagoshima et al., 2015). The mixing models suggest the involvement of 0.5% to 5% of subducted sediments in the CCVC magmatic source (Table 2).

5.4. Sulfur isotopes: predominance of a MORB-type signature

Hydrothermal gases are characterized by the virtual absence of SO2 and the presence of H2S as unique S-bearing gaseous species (Giggenbach, 1980). Therefore, the isotopic composition of H2S can be very important for establishing the origin of S.

MORBs have a \( \delta^{34}S \) of +0.3 ± 0.5‰ (Sakai et al., 1984) with S/He ratio of 4.2 ± 1.2 × 10^4 (Kagoshima et al., 2015). Modern sediments show a large range of \( \delta^{34}S \) values, from −50‰ to +21‰ (Stefansson et al., 2015 and reference therein; Thode, 1991), while water from rain and snow lies at +2‰ to +9‰ (Thode, 1991). The \( \delta^{34}S \) values of arc lavas have been attributed to the recycling of subducted sulfate through subduction zones (Giggenbach, 1992; González-Partida et al., 2005; Matsuda et al., 2005; Stefánsson et al., 2015), while those of high temperature volcanic gases in global arc systems are due to mixing of subducted sulfates and pyrite (Kagoshima et al., 2015). Sulfur isotopic fractionation is common in magmatic and hydrothermal systems (de Moor et al., 2013b; González-Partida et al., 2005; Marini et al., 2011; Matsuda et al., 2005; Stefánsson et al., 2015) and is controlled by various parameters such as the sulfur valence state (gas/melt and vapor/solid), the crystallization of S-bearing minerals, the degassing process, and the temperature (Marini et al., 2011).

The sulfur isotopic compositions are investigated in the CCVC fluids (Fig. 9) ranging from −4.86‰ (TC) to +2.77‰ (LM) and an average of −1.58‰, lighter than those of high temperature volcanic gases with the average of +4.6‰. As similarly observed for geothermal/hydrothermal systems in Japan and Mexico (González-Partida et al., 2005; Matsuda et al., 2005), the CCVC gases have a large range of \( \delta^{34}S \) values, suggesting that the sulfur source composition has been modified in the hydrothermal or magmatic system.

Boiling can have significant effects on the sulfur isotopic composition and S/He ratio in geothermal system. The isotopic compositions of sulfur in over 105 samples of pyrite from five deep wells of the Los Humeros geothermal field, Mexico, were determined by Martinez Serrano et al. (1996) along with the \( \delta^{34}S \) values of dissolved sulfate and sulfate. The \( \delta^{34}S \) values of pyrite and H2S are similar and vary between...
values strongly depleted in $^{34}$S observed in pyrites from shallow levels of geothermal reservoirs coming from deep zones, where boiling does not occur, with compositions of hydrothermal pyrite in the Los Azufres geothermal field. Another study from González-Partida et al. (2005) reported the isotopic values of pyrite from four wells, with an average of $-4.8\%_\nu$. Modern sediment and Rain-Snow data from Marini et al. (2011) and Thode (1991). Subducted sulfate and sedimentary pyrite are defined by Kagoshima et al. (2015).

- $-4.5$ and $+4.5\%_\nu$, around an average of $+0.02\%_\nu$, suggesting that the provenance of sulfur involves a magmatic source. However, the $^{34}$S values of pyrite from four wells, with an average of $-0.4\%_\nu$, are slightly more negative than those from the fifth borehole, with a mean of $+2\%_\nu$. The largest changes in the isotopic characteristics of pyrite and $H_2S$ were observed at depths where boiling and mixing phenomena occur. Another study from González-Partida et al. (2005) reported the isotopic compositions of hydrothermal pyrite in the Los Azufres geothermal field. Two different groups were identified: (1) the pyrite samples coming from deep zones, where boiling does not occur, with $^{34}$S values of $-1.6$ to $-3.0\%_\nu$, and (2) the pyrites sampled from steam-dominated at shallow levels, with $^{34}$S values of $-4$ to $-4.8\%_\nu$. The average $^{34}$S value of pyrite, $-2.5\%_\nu$, is similar to that of $H_2S$, $-2.0\%_\nu$. The authors suggested that: (1) the initial isotopic value for sulfur in the geothermal reservoir, $-2.3\%_\nu$, implies a magmatic source; and (2) the values strongly depleted in $^{34}$S observed in pyrites from shallow levels are produced by fractionation during boiling of hydrothermal fluids.

Considering the large range of $^{34}$S values observed in Copahue geothermal fluids ($-4.8\%_\nu$ to $+2.77\%_\nu$) and the conclusions of these two previous studies, we could argue for the sulfur fractionation by boiling process in the geothermal reservoir from Copahue. Another argument for this conclusion is the particular large change in sulfur composition from vent to vent that suggests that the effects of shallow processes on the $^{34}$S value of $H_2S$ are important. In this condition, it is difficult to access the magmatic composition of Copahue geothermal fluids. Previous authors (Agusto et al., 2013; Varekamp et al., 2009) have been suggested that the well COP-2 has a composition representative of the magmatic-hydrothermal system. In this way, the sulfur composition of Copahue magmatic system will be $-2.38\%_\nu$, however, this sample seems to be also affected by part of boiling separation process as it was showed with elemental noble gas previously. In the future, the $^{34}$S value of total sulfur could be coupled together with $S/H_2S$ ratio to provide another information as it was proposed by Kagoshima et al. (2015).

5.5. Isotopic composition of the CCVC fluids versus tectonic features

In the Andean SVZ, geothermal activity occurs in close spatial relationships with active volcanism along the Cordillera, which is primarily controlled by the $-1000$ km long, NNE-trending Liquiñe-Ofqui Fault Zone (LOFZ), an intra-arc dextral strike-slip fault system associated with second-order anisotropy of overall NE-SW (extensional) and NW-SE (compressional) orientation (Fig. 1) (Cembrano et al., 1992, 1996, 2000; Cembrano and Lara, 2009). Rosenau et al. (2006) proposed that the particular location of CCVC is the result of the NE-striking extensional and transtensional faults that form an accommodation zone arrangement with a horse tail-like geometry; in brittle terminations, the displacement is distributed through several branching splay faults. These small faults, curved away from the strike of the main fault, form an open imbricate fan. These structures, due to their high permeability, promote the formation of vertical fluid pathways (Rowland and Simmons, 2012) in favor of geothermal and hydrothermal system appearance.

Fig. 9. $^{34}$S of the CCVC fluids compared to other volcanic arc data and the MORB end-member (Giggenbach, 1992; González-Partida et al., 2005; Matsuda et al., 2005; Stefansson et al., 2015). Modern sediment and Rain-Snow data from Marini et al. (2011) and Thode (1991). Subducted sulfate and sedimentary pyrite are defined by Kagoshima et al. (2015).

Fluids from Pucon Mahuida have high $Rc/Ra$ ($-6.4Ra$), low $^{13}$C-CO$_2$ ($-11.1\%$), and high $^{15}$Nc ($-4.2\%$), consistent with a mixing between volcanic fluids (magmatic-hydrothermal) and local organic sediments. This is consistent with the inferred NE fault network that has been reported by Rojas Vera et al. (2009).

The Chancho-co fluids are characterized by moderate $Rc/Ra$ ($4.18Ra$ to $5.19Ra$) and low $^{13}$C ($-1.1\%$), $^{13}$C-CO$_2$ ($-9.0\%$), $d^2$H$_2O$, and $^{18}$O-$H_2O$. They also have high $H_2S$ ($S_{total}$ as $H_2S$ only) and $H_2$, along with low $C_5$ contents (Table 1). All these geochemical features suggest important dilution of the magmatic source by meteoric water and contamination by local organic sediments during water-rock interaction. This is consistent with the location of Chancho-co along a major
WNW fault considered inefficient for hydrothermal fluid ascent but efficient for meteoric water infiltration (Rouleau et al., 2015a, 2016). H2S is directly linked to the volcanic activity; it is commonly observed in volcanic and geothermal areas. However, the high H2S contents of Chancho-co samples cannot be only related to its volcanic origin. H2S is also formed by the decomposition of organic material by bacteria. This process is inferred to be part of the H2S source for the Chancho-co fluids and should be verified by Stotal/3He in the future.

In summary, we provide insights here that the CCVC structures control the geochronal and isotopic features of the fluids and hence, the whole geothermal system. Of particular importance are the NE faults that are thought to be direct pathways for fluid circulation from the magmatic source up to the surface.

6. Conclusions

We measured noble gas (He, Ne, Ar, Kr, and Xe) and stable (δD, δ15N, δ18O, and δ34S) isotopes in several geothermal and hydrothermal samples from the CCVC. The goal of this work was to provide insights into the fluid circulation and evolution of this hydrothermal/geothermal system as controlled by the activity of Copahue volcano and the local structures. With the exception of Anfiteatro (up to 5.39Ra), the northeastern geothermal fields, composed of Las Maquinas, Las Maquinitas, Termas de Copahue, and Cabanita, provide the highest R/Ra in the studied area and in the entire SVZ (up to 7.86Ra in 2015). The hydrothermal activity observed at Pucón Mahuida (southern flank of Copahue volcano) and Chancho-co (northern flank of the volcano) exhibits moderate to low 3He/4He (up to 6.59Ra and up to 5.19Ra, respectively). The high elemental ratios of Xe and Kr observed for most CCVC gas samples are explained by elemental fractionation during boiling and steam separation at hydrothermal temperatures (250–300 °C). Rayleigh distillation curves simulate the CCVC fluid evolution, considering an initial ASGW of 250 °C and a temperature of 300 °C followed by boiling and steam separation at lower temperature, from 200 °C to 150 °C. The low 3He/4He ratios are largely explained by meteoric water and air contamination, which follow the boiling-steam separation event. The hydrogen and oxygen isotopes present an increase from meteoric water to andesitic water signature between 2014 and 2015. This evolution is also associated with an increase of δ13C values and Stotal, HCl, and He contents, along with a decrease of CO2/3He inferred to be the result of a change in the path of gas uprising, in turn inducing higher magmatic-hydrothermal contribution in the fluid signature. The composition of the magmatic source of the CCVC fluids is: 3He/4He = 7.7Ra, δ15N = + 6‰, and δ13C = − 6.5‰. Mixing models between air-corrected He and N suggest the involvement of 0.5% to 5% of subducted sediments in the CCVC magmatic source. The magmatic sulfur isotopic composition is estimated at − 2.38‰ (from COP-2), but most samples show elemental fractionation due to boiling and steam separation. The geochemical and isotopic features of the CCVC fluids illustrate the particular structural setting observed in this volcanic and geothermal area. NE faults promote the ascent of hydrothermal fluids in the geothermal area whereas WNW faults serve as preferential channels for meteoric water infiltration.

Acknowledgements

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### Table A1

#### Ne, Kr, Ar and Xe isotopic ratios.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Field zone</th>
<th>Type</th>
<th>$^{20}\text{Ne}/^{22}\text{Ne}$</th>
<th>$^{21}\text{Ne}/^{22}\text{Ne}$</th>
<th>$^{38}\text{Ar}/^{36}\text{Ar}$</th>
<th>$^{40}\text{Ar}/^{36}\text{Ar}$</th>
<th>$^{80}\text{Kr}/^{84}\text{Kr}$</th>
<th>$^{82}\text{Kr}/^{84}\text{Kr}$</th>
<th>$^{83}\text{Kr}/^{84}\text{Kr}$</th>
<th>$^{40}\text{Kr}/^{84}\text{Kr}$</th>
<th>$^{86}\text{Kr}/^{84}\text{Kr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>Chanco-co</td>
<td>Fumarole</td>
<td>9.5786</td>
<td>0.0170</td>
<td>0.0285</td>
<td>0.0001</td>
<td>0.1879</td>
<td>0.0002</td>
<td>294.7</td>
<td>0.0062</td>
<td>0.0002</td>
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<td>Anfiteatro</td>
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<td>0.0292</td>
<td>0.0001</td>
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<td>0.0369</td>
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<td>Cabañitas</td>
<td>Fumarole</td>
<td>9.9016</td>
<td>0.0221</td>
<td>0.0292</td>
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<td>0.1882</td>
<td>0.0003</td>
<td>301.1</td>
<td>0.0371</td>
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</tr>
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#### Table A1 (continued)

Ne, Kr, Ar and Xe isotopic ratios.

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<th>$^{129}\text{Xe}/^{130}\text{Xe}$</th>
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