Exploring the structural controls on helium, nitrogen and carbon isotope signatures in hydrothermal fluids along an intra-arc fault system

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Abstract

There is a general agreement that fault-fracture meshes exert a primary control on fluid flow in both volcanic/magmatic and geothermal/hydrothermal systems. For example, in geothermal systems and epithermal gold deposits, optimally oriented faults and fractures play a key role in promoting fluid flow through high vertical permeability pathways. In the Southern Volcanic Zone (SVZ) of the Chilean Andes, both volcanism and hydrothermal activity are strongly controlled by the Liquiñe-Ofqui Fault System (LOFS), an intra-arc, strike-slip fault, and by the Arc-oblique Long-lived Basement Fault System (ALFS), a set of transpressive NW-striking faults. However, the role that principal and subsidiary fault systems exert on magmatic degassing, hydrothermal fluid flow and fluid compositions remains poorly constrained. In this study we report new helium, carbon and nitrogen isotope data (\(^{3}\)He/\(^{4}\)He, \(\delta^{13}\)C–CO\(_{2}\) and \(\delta^{15}\)N) of a suite of fumarole and hot spring gas samples from 23 volcanic/geothermal localities that are spatially associated with either the LOFS or the ALFS in the central part of the SVZ. The dataset is characterized by a wide range of \(^{3}\)He/\(^{4}\)He ratios (3.39 Ra to 7.53 Ra, where Ra = \(^{3}\)He/\(^{4}\)He\(_{air}\)), \(\delta^{13}\)C–CO\(_{2}\) values (−7.44‰ to −49.41‰) and \(\delta^{15}\)N values (0.02‰ to 4.93‰). The regional variations in \(^{3}\)He/\(^{4}\)He, \(\delta^{13}\)C–CO\(_{2}\) and \(\delta^{15}\)N values are remarkably consistent with those reported for \(^{87}\)Sr/\(^{86}\)Sr in lavas along the studied segment, which are strongly controlled by the regional spatial distribution of faults. Two fumaroles gas samples associated with the northern “horsetail” transensional termination of the LOFS are the only datapoints showing uncontaminated MORB-like \(^{3}\)He/\(^{4}\)He signatures. In contrast, the dominant mechanism controlling helium isotope ratios of hydrothermal systems towards the south appears to be the mixing between mantle-derived helium and a radiogenic component derived from, e.g., magmatic assimilation of \(^{4}\)He-rich country rocks or contamination during the passage of the fluids through the upper crust. The degree of \(^{4}\)He contamination is strictly related with the faults controlling the occurrence of volcanic and geothermal systems, with the most contaminated values associated with NW-striking structures. This is confirmed by \(\delta^{15}\)N values that show increased mixing with crustal sediments and meteoric waters along NW faults (AFLS), while \(\delta^{13}\)C–CO\(_{2}\) data are indicative of cooling and mixing driving calcite precipitation due to increased residence times along such structures. Our results show that the structural setting of the region exerts a first-order control on hydrothermal fluid composition by conditioning residence times of magmas.

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and thus promoting cooling/mixing of magmatic vapor, and therefore, must be taken into consideration for further geochemical interpretations.

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### 1. INTRODUCTION

In arc settings, helium isotopes have been successfully used, coupled with stable isotopes of carbon and nitrogen data, to constrain mantle heterogeneities and mechanisms of volatile recycling (Sano and Marty, 1995; Sano and Williams, 1996; Fischer et al., 1998, 2002; Sano et al., 2001). Subduction zones represent one of the preferential regions to study such contributions, coupled with stable isotopes of carbon and nitrogen (Sano and Marty, 1995; Sano and Williams, 1996; Fischer et al., 1998, 2002; Sano et al., 2001). Such studies have proved critical to constrain the relative mantle vs. subducted sediment contributions on the isotopic signature of hydrothermal fluids, as well as the degree of contamination by upper crustal rocks. Despite these significant advances, very few studies have focused on deconvolving the regional scale structural and tectonic controls affecting the composition of deep-seated fluids during the separation from the magmatic source and the passage through the crust (Kennedy et al., 1997; Kennedy and van Soest, 2005; Karlstrom et al., 2013). In particular, the local scale control of interconnected faults and associated fractures (fault-fracture meshes; Sibson, 1996) on fluid flow in geothermal and hydrothermal systems has been largely studied over the past twenty years (Sibson, 1994, 1996; Manning and Ingebritsen, 1999; Sibson and Rowland, 2003; Fairley and Hinds, 2004; Micklethwaite and Cox, 2004; Rowland and Sibson, 2004; Blenkinsop, 2008; Graf and Therrien, 2009; Cox, 2010; Faulkner et al., 2010; Gudmundsson et al., 2010; Micklethwaite et al., 2010; Rowland and Simmons, 2012). These studies have improved our understanding about the structural factors controlling fluid flow, and have provided crucial information to refine conceptual models of the local fault-fracture hydraulic architecture in geothermal and hydrothermal systems.

The goal of this study is to unravel the regional scale structural controls on the isotopic composition of subduction-related magmatic gas, from its source to their pathway toward the surface. Our aim is to assess the nature of the link among fault-fracture meshes, magmatic degassing, crustal assimilation and fluid mixing processes taking place in the upper crust, that affect the composition of hydrothermal fluids discharged along principal and subsidiary structures of a regional scale, intra-arc strike slip fault. Considering the fact that tectonic activity defines the nature, geometry and kinematics of fault-fracture networks, a better understanding of the structural pattern and its link with the chemical evolution of fluids may give significant insights into the processes governing the dynamics of hydrothermal systems associated with such large-scale crustal structures.

The Andean Cordillera of Central-Southern Chile is a perfect natural laboratory to test this hypothesis. In this region, the relationship between tectonics and volcanism is the result of interaction between the crustal structures of the basement and the ongoing regional stress field (Pritchard et al., 2013). As pointed out by several studies, magmatism and volcanism, as well as geothermal activity in the region are spatially associated with tectonic features (Hildreth and Moorbath, 1988; López-Escobar et al., 1995; Hauser, 1997; Pérez, 1999; Sepúlveda et al., 2004; Lara et al., 2006; Cembrano and Lara, 2009; Alam et al., 2010; Lahsen et al., 2010; Sánchez et al., 2013). In particular, in the Southern Volcanic Zone (SVZ) between 37° and 46°S, the volcanic and geothermal activity is partially controlled by the ∼1000 km long, NNE-striking intra-arc dextral strike-slip Liquine-Ofqui Fault System (LOFS), and by the NW-SE Arc-oblique Long-lived Basement Fault System (ALFS). Many geothermal surface manifestations and shallow fumarolic emissions are spatially related to stratovolcanoes and fault segments associated with both fault systems (Fig. 1).

Previous geochemical surveys conducted in this region have recognized a wide range of 3He/4He ratios in volcanic/geothermal fluids, suggesting mixing between mantle helium and the radiogenic helium sourced from country rocks (Hilton et al., 1993; Ray et al., 2009; Dobson et al., 2013). However, these studies have focused either on orogen-scale controls on noble gas compositions, or have addressed the local structural controls in individual geothermal systems (Sepúlveda et al., 2007; Agusto et al., 2013). In this study we present a comprehensive dataset of helium, nitrogen and carbon isotope analyses from a suite of about 20 volcanic fumaroles and thermal springs between the 37° and 41°S. The gas samples were collected from fumaroles in active volcanic systems and thermal springs that are closely spatially associated with both the LOFS and the ALFS. Based on new and unpublished mapped structures and as a up-to-date structural background in the region (Potent, 2003; Melnick et al., 2006; Lara et al., 2006; Cembrano and Lara, 2009; Pérez-Flores et al., 2014), we highlight the role of LOFS and ALFS on fluid circulation and provide a new interpretation that explains the spatial variations of helium, nitrogen and carbon isotopes in thermal fluids in the Central Southern Volcanic Zone of Chile.
2. GEOLOGICAL AND STRUCTURAL SETTING

The Southern Volcanic Zone (SVZ) of south-central Chile lies between 33°S and 46°S (Fig. 1). Along with the Central Volcanic Zone (CVZ, 14–28°S) and the Austral Volcanic Zone (AVZ, 49–55°S), it constitutes a three-segment active arc that comprises the Chilean Andes (Parada et al., 2007; Stern et al., 2007).

The Andean region examined in this study is about 450 km-long (37°–41°S), and forms part of the central and southern segments of the Southern Volcanic Zone (SVZ) (Fig. 1). In this region, the current geodynamic
setting is characterized by slightly oblique convergence between the Nazca and South American plates at a rate of ca. 7–9 cm/year that has prevailed for the last 20 Ma (Angermann et al., 1999; Somoza and Ghidella, 2005). The basement of the volcanic arc, in the northern portion of this segment at 39°S, is made up of extensive outcrops of the Meso–Cenozoic volano-sedimentary rocks of the Cura Mallin and Cola de Zorro formations, which are locally intruded by Mio–Pliocene plutons (Charrier et al., 2002). South of 39°S, recent volcanic edifices are built directly on Meso–Cenozoic plutonic rocks of the Patagonian Batholith. Crustal thickness underneath the volcanic arc decreases from 50 km at 33°S to 35 km at 46°S, with an accompanying decrease in the average altitude of the main cordillera, from 5000 m to less than 2000 m (Tassara and Yáñez, 2003).

The structural setting of the studied segment in Fig. 1 is dominated by the Liquine-Ofqui Fault System (LOFS), a NNE-striking, intra-arc transpressional dextral strike-slip fault system that extends between 37°S and 46°S, and associated with ENE-striking second-order intra-arc anisotropies (Cembrano et al., 1996, 2000; Folguera et al., 2002; Adriasola et al., 2006; Rosenau et al., 2006). The ENE-striking structures have been recognized as extensional fractures most likely formed under relatively low differential stress (Lavenu and Cembrano, 1999; Cembrano and Lara, 2009). Conversely, the arc oblique WNW-striking long-lived basement fault system (ALFS) is severely misoriented with respect to the prevailing stress field, and has been interpreted as crustal weaknesses associated with pre-Andean faults reactivated as sinistral-reverse strike–slip faults during the development of the arc (Cembrano and Moreno, 1994; López-Escobar et al., 1995; Lara et al., 2006; Melnick et al., 2006; Rosenau et al., 2006; Glodny et al., 2008; Lange et al., 2008).

The volcanism in the segment is represented by stratovolcanoes and monogenic cones, many of which are spatially associated with the LOFS or ALFS. Their composition is mainly basaltic-andesitic with minor dacitic-rhyolitic occurrences. The stratovolcanoes and/or monogenic cones exhibit mostly primitive magmatic signatures, and are related to secondary structures forming NE-trending volcanic alignments which are directly related to the current dextral transpressional tectonic regime (Lara et al., 2006; Cembrano and Lara, 2009). In contrast, the volcanic activity spatially related to the ALFS comprises WNW-trending volcanic alignments, where mostly stratovolcanoes occur. These include a wide range of compositions, with some centers having erupted only rhyolitic products in historical times. Because of their misorientation with respect to the prevailing stress field, the WNW-striking faults require supralithostatic magmatic pressures to become active (see Lara et al., 2004, 2006; Cembrano and Lara, 2009).

The northern segment of the LOFS (37.5–39°S) is characterized by transtensional deformation and shows an accommodation zone individuated by fault splays and graben formation. At 37.5°S, the interaction of the Liquine-Ofqui fault and the Copahue-Antinir fault results in a NE-striking transitional zone (Melnick et al., 2006). At 38°S, the N–S to NNE-striking LOFS bends eastward and decomposes into a series of NE-striking extensional and transtensional fault splays that form an arrangement characterized by a “horsetail”-like geometry (Potent and Reuther, 2001; Rosenau et al., 2006). These types of structures have long been recognized to play a key role as host structures and high-permeability flow paths for geothermal systems and hydrothermal mineralization (Sibson, 1994, 1996; Rowland and Sibson, 2004; Rowland and Simmons, 2012).

### 3. Sampling and Analytical Techniques

Gas and water samples were collected from fumaroles in active volcanic systems, bubbling hot springs and thermal water springs. Fumarole gases were sampled using a titanium tube, inserted into the fumarole or vent, and connected to a condenser and a water separator, to force water condensation. The dry gas obtained was collected in pre-evacuated alkaline glass containers with vacuum valves at both ends. Water and bubbling gas from hot springs were sampled in double valve, pre-evacuated alkaline glass containers, using pure silicone tubes connected to an inverted funnel and a manual pump. Dissolved gases from thermal water samples were extracted using a glass bottle under vacuum in the extraction line. Both methods for volcanic gases and water spring/bubbling gases are exhaustively described in Sano and Fischer (2013).

The ³He/⁴He ratios were measured using a noble gas mass spectrometer (Helix-SFT) at the Atmosphere and Ocean Research Institute (AORI), University of Tokyo, Japan. The ⁴He/²⁰Ne ratios were measured using a quadrupole mass spectrometer. Helium and neon were separated using a cryogenic trap operated at 40 K (see Sano and Wakita, 1988). The measured ³He/⁴He ratios were calibrated against atmospheric helium. Experimental errors of ⁴He/²⁰Ne and ³He/⁴He ratios are about 0.5% and 1% at 1σ, respectively (Sano et al., 2006). Assuming that the Air Saturated Water (ASW) neon content is significantly higher than in mantle and crustal gases, the R/Ra can be corrected for the presence of atmospheric helium using the ³He/²⁰Ne ratio of the sample (Craig et al., 1978). The error calculation for air corrected helium was performed using the procedure described in Sano et al. (2006).

The δ¹³C and δ¹⁵N values of gas samples were measured using a conventional gas source mass spectrometer (Isoprime100, Isoprime Ltd.) at AORI. All values were corrected for blanks that represent 0.2% of the measurement contribution (Barry et al., 2012). The error of the delta values is the propagated error of the isotopic measurement of N and C in the sample, the standard and the blank, assumed at 1σ. The carbon isotopic composition was measured in CO₂ and CH₄ gaseous component and is expressed in delta notation as:

\[ \delta^{13}C = \left( \frac{^{13}C/^{12}C_{\text{sample}}}{^{13}C/^{12}C_{\text{STD}}} - 1 \right) \times 1000 \]

The nitrogen isotopic composition is given by:

\[ \delta^{15}N = \left( \frac{^{15}N/^{14}N_{\text{sample}}}{^{15}N/^{14}N_{\text{air}}} - 1 \right) \times 1000 \]
The chemical composition (He, CH₄, N₂, O₂, Ar, H₂S and CO₂) of sampled gases was measured using a quadrupole mass spectrometer at AORI, by comparing peak heights of the sample with those of standard gases. Experimental errors were estimated to be about ±10% by repeated measurements of standard samples. The blank for each component was significantly lower compared to the sample signals.

4. RESULTS

Tables 1 and 2 present the chemical composition and isotopic data (R/Ra, ²³⁴He/²⁰⁸Ne, air-corrected ³⁶He/³²He (Rc/Ra) ratios, δ¹⁵N, δ¹³C, δ¹³CO₂ and δ¹²C–CH₄ values) of gas samples from 23 volcanic/geothermal localities, including 5 fumaroles, 7 bubbling gas and 11 hot springs (water-dissolved gas). In the tables, samples are sorted in latitudinal order and labeled with a sample name and with an ID label, from 1 to 23, from north to south. Furthermore, for the sake of simplicity, we will refer to samples as fumarole gas and hot spring gas samples. Fig. 1 shows sample locations and their association with the main structural features of the LOFS and ALFS.

4.1. Gas composition

All five fumarole gas samples are dominated by CO₂, representing at least the 80% of the total gas in each sample. For the hot spring gas, the samples AV (5), PE (6), VA (11), QC (14), PA (16), CO (18), TR (19), CH (20), AC (22) and RU (23) are dominated by N₂, while the others are dominated by CO₂, with the exception of the CH₄-dominated TT (2) sample. Methane was also detected in all other samples, with six of them showing concentrations that are higher than 1%. The reduced sulfur compound H₂S was detected in seven samples. The five fumarole gas samples present the highest H₂S concentrations, while PE (6) and PM (4) are the only two hot spring gas where H₂S concentrations are detectable.

The majority of fumarole and hot spring gas samples have O₂ contents lower than 5%, with the exception of four samples (AV (5), RB (13), PU (21) and RU (23)). Three of these samples (RB (13), PU (21) and RU (23)) have N₂/O₂ close to the air ratio, of 3.73, suggesting a significant atmospheric contamination. In contrast, the helium isotope composition was not strongly affected by atmospheric helium in these three samples, suggesting that the contamination has probably happened during analysis. The ³⁶He/²⁰⁸Ne ratios are 1.57, 1.37 and 4.20 respectively, at least four times higher than the air ratio (0.33).

In Fig. 2, the inert (He and Ar) and nearly inert (N₂) gas compositions are plotted in a ternary diagram, and used as a source indicator for the origin of volatile components (after Giggenbach and Goguel, 1989; Giggenbach and Poreda, 1993). The N₂/Ar ratio of the samples varies between 38.73 and 544.73. All samples, with the exception of sample PL (7), roughly fit a mixing trend between arc-derived fluids (“Arc-type sediments”) and a second end-member comprised between the atmospheric value (“Air”) and the Air-Saturated Water value (“ASW”). The presence of atmospheric gases in the mixture is visible in Fig. 2, and is consistent with previously published data by Ray et al. (2009) for the region. Fumarolic outlier gas sample PL (7), instead, shows a mantle-fluid affinity with atmospheric (air) contribution.

The CO₂/³²He ratios were calculated from CO₂/He and ³⁶He/³²He ratios for each sample. The CO₂/³²He ratios for water-dissolved gases and bubbling gases cover an exceptionally wide range between 116.01 × 10⁻⁶ (CU (8)) and 5.08 × 10⁻⁶ (AV (5)) (Fig. 3). More than half of the samples show CO₂/³²He ratios lower than MORB (2.0 ± 1.0 × 10⁻⁶; Marty and Jambon, 1987) and global arc-like values (1.5 ± 1.1 × 10⁻⁶; e.g., Sano and Williams, 1996), in agreement with previous data for the region (e.g., Ray et al., 2009). All fumarolic gas samples range from 17.78 × 10⁻⁶ (NC (1)) to 1.56 × 10⁻⁶ (PL (7)), and are included in the global arc average field (with the exception of sample PL (7) plotting in the MORB field). The hot spring samples PM (4) (57.83 × 10⁻⁶) and CU (8) (116.01 × 10⁻⁶) are the only ones exceeding the global arc average value.

4.2. He, N and C isotope composition

The helium, carbon and nitrogen isotope compositions of thermal manifestations along the SVZ of south-central Chile are highly variable and are not directly correlated with their distance from stratovolcanoes. In contrast, as shown in Fig. 4, the helium, carbon and nitrogen isotopic ratios show remarkably similar latitudinal tendencies, analogous to the trend of ⁸⁷Sr/⁸⁶Sr ratios in lavas of principal stratovolcanoes in the segment. Along-arc variations in strontium isotope composition of volcanic rocks are indicative of variable degrees of crustal contamination, most likely due to intracrustal assimilation (Hildreth and Moorbath, 1988; Hickey-Vargas et al., 1989), and/or source region contamination by subducted continental components (Stern, 1991; Kay et al., 2005). The observed variations in helium, carbon and nitrogen isotopes along the studied segment do not seem to correlate with crustal thickness (Moho depth is represented by the red line in Fig. 4), but rather with the regional distribution of NE- and NW-striking faults (Figs. 1 and 4). This observation is in agreement with the fact that these structures play a first order control on the migration and storage of magmas along the SVZ, as studies by Lara et al. (2006) and Cembrano and Lara (2009) have reported.

4.2.1. ²³⁴He/³²He ratios

The air-corrected ³⁶He/³²He ratios (Rc/Ra), given as multiples of the present-day atmospheric ratio (R_a = 1.382 × 10⁻⁶; Sano et al., 2013; Mabry et al., 2013), range from 3.68 Ra to 7.67 Ra (Table 2). The northern part of the studied segment (~37.5–38.5°S) shows the widest range of Rc/Ra values, (Fig. 4). The highest values were found in two fumarolic gas samples (LM (3) and PL (7)) associated with the transtensional “horsetail” structure in the northern part of the LOFS. High ratios were also found, from north to south, in two bubbling gas samples (PM (4) and CU (8)), in a fumarolic gas sample from the Tolhuaca volcano (JM (9)), and in the bubbling gas sample
<table>
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<th>Sample type</th>
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<th>CH₄</th>
<th>N₂</th>
<th>O₂</th>
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Note: F, fumarole gas; WD, water-dissolved gas; BG, bubbling pool gas.
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Note: CO2/3He is calculated from CO2/He and 3He/4He ratios. Error for 4He/20Ne is 5%.

Note: 3He/4He (Ra) ratios are calculated using 3He/4He of air (1.40 × 10^-8 ccSTP/g).

Note: 3He/4He (Rc/Ra) is the denomination for corrected 3He/4He from 4He/20Ne.
BB (12), associated with the Sollipulli volcano. Rc/Ra values are also high in the southern part of the studied area, where three hot spring gas samples (PU (21), AC (22) and RU (23)), close to Puyehue-Cordon Caulle and Casablanca volcanoes, reach MORB-like values. Accordingly, lavas from stratovolcanoes associated with these high Rc/Ra fumaroles and thermal springs show lower strontium isotope ratios (87Sr/86Sr) reflecting a low degree of crustal contamination of these magmatic volatile sources (Fig. 4).

In contrast, the central part of the studied segment, (~38.5–40°S), as well as the northernmost limit at the Nevados de Chillán volcano (~37°S), show lower helium ratios and a narrower distribution of Rc/Ra values, ranging between 5.42 ± 0.01 Ra and 3.68 ± 0.10 Ra. The stratovolcanoes associated with these manifestations present higher values of 8Sr/86Sr ratio in lavas, indicating a higher crustal assimilation of the deep magmatic system.

4.2.2. Carbon isotopes (δ13C–CO2)

The measured δ13C–CO2 values range from −7.44 ± 0.14‰ to −49.41 ± 0.28‰ (Table 2; Fig. 4). Fumarolic gases have the higher values, ranging between −7.44 ± 0.14‰ and −9.75 ± 0.14‰. LM (3) and PL (4) samples, in particular, have MORB-like (−6.5 ± 2.2‰; e.g., Sano and Marty, 1995) and high temperature volcanic gas (−5.5 ± 2.2‰; e.g., Sano and Marty, 1995; Sano and Williams, 1996) signatures. Hot spring gas samples range between −11.87 ± 0.14‰ and −49.41 ± 0.28‰, except for one sample that has more affinity to a fumarolic gas-like signature (sample CU (8), −7.44 ± 0.14‰).

In agreement with Rc/Ra and 8Sr/86Sr trends, the stable isotopes of carbon (δ13C–CO2) show a regional distribution where the highest (heaviest) values are restricted to the northernmost and southernmost parts of the studied segment. The central part of studied region shows lighter carbon signatures. The lightest value (−49.41‰) corresponds to the bubbling gas sample PA (16) and is coincident with a very low CO2/3He value (6.1 x 109) and with the second lowest Rc/Ra value in the region (3.78 Ra).

4.2.3. Nitrogen isotopes (δ15N)

The δ15N values range from 0.02 ± 0.20‰ to 4.93 ± 0.20‰, in agreement with subduction-zone signatures (−5‰ to +7‰; Fischer et al., 2002; Hilton et al., 2002). The highest δ15N values occur in the northern part and the southernmost part of the studied region. The highest δ15N values, in particular, were measured in the fumarole gas sample LM (3) and the bubbling gas sample PM (4), which are both associated with the Copahue volcano in the northernmost “horsetail” termination of the LOFS. In

![Fig. 2. Ternary plot of the relative N2, He and Ar contents of SVZ fumaroles (red diamond) and hot spring (blue circles) gas samples. The end-member components, i.e., mantle, arc-type, air and Air Saturated Water (ASW) are shown for comparison. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 3. CO2/3He versus He concentration plot of SVZ fumaroles (red diamonds) and hot-spring (blue circles) gas samples. Global arc average (1.5 ± 1.1 x 1010; e.g. Sano and Williams, 1996) and MORB (2.0 ± 1.0 x 109; e.g. Marty and Jambon, 1987) fields are shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)
contrast, all thermal springs in central part of the segment, between 38.5°S and 40°S (and the fumarole gas sample NC (1)) show δ15N ratios near 0‰.

5. DISCUSSION

The isotope data of fumaroles and bubbling gas samples presented here show that fluids in the studied segment are characterized by a wide spectrum of Rc/Ra, δ13C–CO2 and CO2/3He values. As shown in Fig. 4, the isotopic compositions are highly variable along the studied area and can be correlated with strontium isotope data in the region. In particular, the northern and southern parts of the studied region are characterized by more primitive helium (Rc/Ra), carbon (δ13C–CO2) and nitrogen (δ15N) values (Fig. 4). This trend is reversed in the central part of the segment (38.5–40°S), where Rc/Ra, δ13C–CO2 and δ15N values are lower and may be related to secondary processes taking place in the shallow crust.

In the following sections we discuss the possible fractionation processes affecting the helium, nitrogen and carbon isotopic signatures in the region. We evaluate the effects of crustal contamination and meteoric fluid mixing on magmatic volatile compositions during the migration towards the surface, and we explore the link between these processes and the structural/tectonic framework of the region (LOFS and ALFS).

5.1. Crustal assimilation and contamination

Crustal contamination can modify the 3He/4He, CO2/3He ratios and δ15N, δ13C–CO2 values through the addition of radiogenic 3He, N2 and CO2 from crustal rocks (Sano et al., 1998). In the SVZ, previous studies have pointed out that the main control on the measured 3He/4He values is related to a combination of near surface magmatic degassing and crustal contamination of degassed magmas (Hilton et al., 1993, 2002; Ray et al., 2009). However, the aforementioned studies did not address the potential effects of regional and/or local structures on crustal contamination and magmatic degassing. Therefore, the impacts of volcanic-tectonic associations on R/Ra variability remain to be tested.

As shown in Fig. 5, the 3He/4He ratios (R/Ra) of analyzed samples in the studied area range between 3.40 Ra and 7.53 Ra. All the fumarole and hot springs gas samples are significantly higher than purely crustal values (0.05 Ra; e.g. Morrison and Pine, 1955), indicating that the whole segment receives a significant contribution of mantle-derived helium. We calculate that at least 45% of helium in the gas phase is derived from the mantle, representing the baseline of the whole segment (Fig. 5). From Fig. 5, it is evident that well-defined data point clusters may be indicative of variations in the degree of crustal contamination, i.e., coinciding with the different structures that control the volcanic/geo thermal manifestations in the region. For example, the two fumarole gas samples in Copahue (LM (3)) and Pelehue (PL (7)) show the highest R/Ra ratios (7.48 Ra and 7.53 Ra, respectively) and are associated with two fault splays located in the northernmost “horsetail” termination of
the LOFS (Fig. 1). In addition, two hot springs samples (PM (4) and CU (8)) that are associated with the aforementioned fumaroles samples also exhibit high $^{3}$He/$^{4}$He values at 6.16 Ra and 5.89 Ra, respectively. Mixing models show additions of crustally derived He that range between 20% and 25% (Fig. 5).

The fumarole gas sample JM (9), the three bubbling gas BB (12), AC (22), RU (23) and the water-dissolved gas sample PU (21), also present high $^{3}$He/$^{4}$He ratios (6.77 to 4.89 Ra, Table 2). Also, the fumarole gas sample at “Las Sopas”, associated with Cordón-Caulle volcano, fit within the same range, with a $^{3}$He/$^{4}$He ratio of 6 Ra (Sepulveda et al., 2007). As shown in Fig. 5, these samples are characterized by ~15–25% of contamination with crustal helium. All these intermediate to high $R/Ra$ emissions, as shown in Fig. 1, are associated with volcanoes that are controlled by NE-striking extensional faults (e.g., Sollipulli volcano), or by the intersection between NE- and NW-striking faults (Tolhuaca and Puyehue-Cordon Caulle volcanoes). The aforementioned analysis strongly suggests that $R/Ra$ values in fumaroles and hot springs in the studied area are influenced by crustal contamination processes that are at least partially controlled by regional and/or local structures. In the next paragraphs we use $d^{15}$N, $d^{13}$C–CO$_2$ data and mixing models to provide further evidence to support this assumption.

In Fig. 6, the $d^{15}$N is plotted with N$_2$/He (a) and N$_2$/Ar (b) ratios. Nitrogen contribution end members from sediments ($d^{15}$N = +7‰, N$_2$/He = 1.05 x 10$^4$), MORB ($d^{15}$N = −5‰, N$_2$/He = 1.5 x 10$^3$) and air/ASW ($d^{15}$N = 0‰ and N$_2$/He = 1.49 x 10$^3$) are reported in Fig. 6a (from Sano et al., 1998; Ozima and Podosek, 2002; Fischer et al., 2002; Cior et al., 2005). The mixing curves are defined as:

$$d^{15}_{N\text{obs}} = A \times d^{15}_{N\text{air}} + M \times d^{15}_{N\text{MORB}} + S \times d^{15}_{N\text{sed}}$$

where $d^{15}_{N\text{obs}}$, $d^{15}_{N\text{air}}$, $d^{15}_{N\text{MORB}}$ and $d^{15}_{N\text{sed}}$ refer to the observed values of air, MORB and sediments, respectively, while $A$, $M$ and $S$ are the fractions of air, MORB and sediments, respectively.

According to the literature, the N$_2$/He values for volcanic arc samples typically range between 1000 and 10,000, with lowest and highest values reported at 101 and 24,899, respectively (Giggenbach and Corrales, 1992; Giggenbach and Glover, 1992; Giggenbach and Poreda, 1993; Fischer et al., 2002; Clor et al., 2005). These values are significantly higher than those observed in MORBs (N$_2$/He ~ 150; Sano et al., 2001).

The percentage of sediments in the mixture for almost all the samples varies between 88% and 97%, in agreement with gas data from the Copahue volcano (Agusto et al., 2013). Sample PL (7) at Pelehue deviates the general trend, accordingly with the He-N$_2$-Ar diagram in Fig. 2, and shows a more pronounced MORB signature with only a 55% contribution from the sediments endmember. This signature is also confirmed by the corrected $^{4}$He/$^{3}$He ratio with the highest value in the region (7.67 Ra) representing a MORB-like signature (Figs. 4 and 5).

It is noteworthy to mention that at least part of this nitrogen can be also derived from crustal sources such as shallow or deeply buried sediments and added to fluids during their migration towards the surface (Mitchell et al., 2010). However, it is difficult to obtain precise information about crustally derived nitrogen because the N$_2$/He ratios of our samples are fractionated by air contamination. Despite these limitations, we calculate the fraction of sediment-derived and MORB-derived nitrogen using the following relation (e.g. Fischer et al., 2002):
$\delta^{15}N_c = (1 - f_{\text{sed}})\delta^{15}N_{\text{MORB}} + f_{\text{sed}}\delta^{15}N_{\text{sed}}$

where $\delta^{15}N_c$, $\delta^{15}N_{\text{MORB}}$, $\delta^{15}N_{\text{sed}}$ are the corrected, MORB ($-5 \pm 2\%$) and sediments ($+7 \pm 4\%$) $\delta^{15}N$ values (Sano et al., 2001; Ozima and Podosek, 2002; Table 2). $f_{\text{MORB}}$ and $f_{\text{sed}}$ are the fractions of MORB-derived and sediment-derived nitrogen, respectively. In Fig. 7, the calculated $\delta^{15}N_c$ values were plotted as a function of $R_c/R_a$ ratios. The air-corrected nitrogen values range between 1.60 (sample PL (7)) and 6.64 (sample PE (6)) and fit in the mixing line between MORB and sediments. Samples PL (7) and PL (7) show MORB-like signature consistent with a deep source for carbon. All the other fumarole gas samples (NC (1), JM (9), BT (10)) and four hot spring gas samples (PM (4), CU (8), VA (11), RB (13)) fall in a mixing field between MORB and crustal sediments, showing an important contribution of carbon from crustal sediments (Fig. 8). All the other bubbling gas and water-dissolved gas samples plot outside the mixing trend and show fractionation with relative loss of the heavier isotope that correlates with radiogenic $^4\text{He}$ addition.

The $\delta^{13}C$ values (e.g., Fig. 3) are lower than global arc average in most of the hot springs samples, with a minimum value at 5.08 $\times 10^4$. Those low $\delta^{13}C$ values and the carbon isotope fractionation trend observed in the region seem to be controlled by secondary processes affecting the magmatic/hydrothermal systems, and that can drive the relative loss of $\text{CO}_2$ and a decrease in the $\delta^{15}N$ values (e.g., Fig. 8). Magmatic degassing and calcite precipitation may be responsible for such modifications on the isotopic composition of carbon; in fact, Ray et al.
(2009) hypothesized that these two processes are currently affecting geothermal emissions in the SVZ, with a stronger influence in the volatile-poor, hot-spring samples. As suggested by the correspondence between $R_c/R_a$ values and $\delta^{13}C$ and $CO_2/3He$ ratios (Fig. 8), magmatic degassing and calcite precipitation may be linked to increased residence times of fluids and crustal assimilation of the magmatic source (magmatic degassing). Therefore, it is likely that structurally-controlled vertical permeability exerts a significant role in modulating residence (and thus reaction) times of migrating fluids, conditioning their geochemical and isotopic signature through degassing or mixing with meteoric water (leading to calcite precipitation). These two processes will be discussed more precisely in further sections.

5.2. Mixing with meteoric fluids

As reported in previous studies (e.g., Sánchez et al., 2013), mixing with meteoric waters is one of the main processes affecting the chemical and isotopic signature of hydrothermal fluids in the SVZ. This process impacts the $^{3}He/^{4}He$ and $\delta^{15}N$ values by the addition of radiogenic $^{4}He$ and $N_2$, directly from atmospheric gases or from air-saturated water (ASW).

In Fig. 5, the $R/Ra$ ratios are plotted along with $^{4}He/^{20}Ne$ ratios. The $^{3}He/^{4}He$ values are indicative of mixing between a MORB-like gas source, with addition of radiogenic $^{4}He$ by crustal contamination and air/air-saturated water (ASW). Bubbling gas and water-dissolved gas from hot springs samples in the southern part of the study area (38.5–40°S), and the fumarole gas sample NC (1) (Nevados de Chillan volcano in the northernmost part of the study area, Figs. 1 and 4) show in general a higher degree of contamination by air/ASW. Samples CU (8), VA (11), RB (13), QC (14), ME (15), PA (16), PF (17), CO (18), TR (19), CH (20) fall in a range between 6% and 20% of meteoric fluids in the mixture. Samples CU (8), PU (21) and RU (23), from the northern and southern part of the segment also fall within the same range. Samples PU (21) and RU (23), as commented above, have probably undergone direct air contamination during sampling. All other fumaroles and hot springs gas samples from the northern (37.5–38.5°S) and southern (41–42°S) segments present a degree of contamination that is significantly lower (<5%).

As we showed in the previous section, the $N_2/He$ and $N_2/Ar$ ratios in fumaroles and thermal fluids in the studied area cover an exceptionally wide range between 767.52 and $6.7 \times 10^4$, and 544.73 and 38.73 respectively. These ratios, when plotted along with $\delta^{15}N$ in Fig. 6a and b, show significant mixing with the atmospheric component. In Fig. 6b, datapoints show a wider dispersion in the mixing with air-derived nitrogen. The hot springs samples between 38.5°S and 40°S and the fumarole gas sample NC (1) show the highest degree of contamination by Air/ASW (Fig. 6b), in agreement with helium isotope data shown in Fig. 5.

Within a hydrothermal system, gas separation has the potential to fractionate both the gas ratio ($CO_2/3He$) and the $\delta^{13}C$–$CO_2$ value (Giggenbach and Poreda, 1993; Barry et al., 2013). The observed $CO_2/3He$ ratios in gas and water are different and consistent with gas separation. Helium is preferentially partitioned into the gas phase, whereas the more soluble $CO_2$ is concentrated in the aqueous liquid. This physical process produces an increase of $CO_2/3He$ in residual water and can induce isotopic fractionation of $13C/12C$ ratios towards lower $\delta^{13}C$–$CO_2$ values (Vogel et al., 1970). As shown in Fig. 3, two bubbling gas samples (PM (4), CU (8)) show higher $CO_2/3He$ values ($5.78 \times 10^{10}$ and $11.6 \times 10^{10}$) compared with their associated fumaroles in the Copahue and Pelehue geothermal areas (LM (3), PL (7)). These values suggest He loss or $CO_2$ addition from local sediments. Furthermore, sample CU (8) has a $\delta^{13}C$–$CO_2$ value (~7.75‰) within the range of arc fumarolic.
gases (Sano and Marty, 1995), while PM (4) show a lower value (−11.87‰). Both samples have an Rc/Ra ratio of 6.23 (PM (4)) and 6.69 (CU (8)) suggesting only a minor degree of crustal contamination. Therefore, the high CO₂/³He ratios may reflect both crustal contamination and/or vapor liquid partitioning processes, in close relation with the local scale fault-fracture meshes controlling the permeability in the Copahue and Pelehué geothermal systems (see Fig. 1).

5.3. Degassing and calcite precipitation

Figs. 3 show that more than half of the hot spring gas samples present low CO₂/³He ratios, in comparison to fumarole samples. This observation, also reported in previous studies in the SVZ (e.g., Ray et al., 2009), is suggestive of CO₂ loss from the magmatic/hydrothermal system (Giggenbach and Poreda, 1993). Ray et al. (2009) proposed two mechanisms that can possibly explain the low CO₂/³He ratios observed in SVG samples: (1) Magma degassing and (2) CO₂ loss driven by calcite precipitation. In the next paragraphs we evaluate these two processes for the studied segment.

Degassing of an andesitic-basaltic magma can produce a decrease in CO₂/³He in residual melt as well as the δ¹³C values (Javoy et al., 1978; Hilton et al., 1998). For the He–CO₂ elemental fractionation, the fractionation factor (α) is defined as (CO₂/³He)⁰/³He(CO₂/³He)₀, i.e., the inverse ratio of the solubility of He and CO₂ in the parental melt. For a tholeiitic melt, α is ~2.35 (Hilton et al., 1998). A preferential loss of CO₂ occurring during melt degassing will cause a decrease in the CO₂/³He ratio for the gas remaining in the melt, and a simultaneously decrease in the δ¹³C values of the residual CO₂ (isotopic fractionation factor proposed is −4‰ corresponding to α: 0.996 Javoy et al., 1978).

Two models of degassing have been proposed: batch equilibrium (closed system) and Rayleigh distillation (open system). For these two models we assume an initial CO₂/³He of 11.95 × 10⁸ and a δ¹³C value of −8.95‰, corresponding to the average CO₂/³He and δ¹³C values of the four fumarole gas samples falling in the volcanic-arc field in Fig. 3. By using the Rayleigh distillation equation, CO₂/³He(Residual) = (CO₂/³He(initial) × F(¹³C(initial)−¹³C_res)) we calculate that the system would have needed to undergo a complete loss of CO₂ to achieve the lower CO₂/³He ratios measured in our samples (i.e., CO₂/³He = 5.08 × 10⁸). Moreover, all our samples that have suffered a relative loss of CO₂ are below the Rayleigh distillation degassing curve in Fig. 9 (labeled “Rayleigh”). Therefore, it is likely that this process does not explain the low CO₂/³He ratios observed in the studied segment. Similarly, we tested a case of batch equilibrium degassing using the equations δ¹³C residual = δ¹³C initial + [(1 − F) × 1000n(ε)], and CO₂/³He residual = (CO₂/³He(mineral) × F(¹³C(residual)−¹³C_initial)) (after Javoy et al., 1978; Ray et al., 2009). As shown in Fig. 9, the batch degassing curve does not fit our data (labeled “Batch”). With this particular mode of degassing, the minimum possible values for CO₂/³He and δ¹³C are 5.0 × 10⁸ and −13‰, respectively (Fig. 9).

Consequently, and in agreement with previous studies by Ray et al. (2009) in the SVZ, we dismiss magmatic degassing as a viable process to explain the lower-than-arc-average CO₂/³He values in our samples. Another alternative mechanism to explain such low CO₂/³He values is CO₂ loss by calcite precipitation, occurring during cooling/mixing history of the hydrothermal system (e.g., Hilton et al., 1998). Fractionation between CaCO₃ and CO₂ gas can be calculated theoretically, and the temperature dependence for C soluble species with respect to CaCO₃ is well constrained (Bottinga, 1969). At temperatures less than 192 °C, calcite is enriched in ¹³C relative to residual CO₂, thus the fractionation factors are −3‰ at 100 °C and −10‰ at 25 °C (Chacko et al., 2001). However, at temperatures greater than 192 °C, calcite is depleted in ¹³C relative to residual CO₂ and the fractionation factor is around 0‰ (Sano and Marty, 1995; Ray et al., 2009; Barry et al., 2014). In Fig. 9, the plotted CO₂/³He and δ¹³C–CO₂ values illustrate the potential effect of calcite precipitation at two different temperatures, 25 °C and 192 °C (dashed lines). Our samples fall in a field defined by these two lines, showing that the low CO₂/³He and δ¹³C–CO₂ values measured in the studied samples can be explained by precipitation of calcite at various temperatures between 25 and 192 °C, as also previously proposed by Ray et al. (2009).

Furthermore, evidence of calcite precipitation is present in several outcrop-scale dilational jogs along master and subsidiary faults of the LOFS (e.g., Pérez-Flores et al., 2014). The only two hot spring samples that do not fit this trend are BB (12) and PF (17). These samples were possibly subjected to hydrothermal degassing processes before calcite precipitation; therefore, these two samples may mark a starting point for the calcite precipitation lines which can be defined, as a first approximation, between the global arc-average and samples PM (4) and CU (8).

5.4. Conceptual model of fluid circulation

By combining the volcano-tectonic association of the studied segment of the SVZ (Table 3) with the helium, carbon and nitrogen isotope data presented in this study, a conceptual model that summarizes fluid circulation in the central part of SVZ is presented in Fig. 10.

The northern termination of the LOFS is characterized by a well-developed “horse-tail”-like accommodation zone (Fig. 1). The associated accommodation zone of such fault architectures, as asserted by many authors (Sibson, 1994, 1996; Kim et al., 2004; Rowland and Sibson, 2004; Rowland and Simmons, 2012), promote high vertical permeability and have long been recognized to play a key role as host structures focusing increased fluid flow in geothermal/hydrothermal systems. In the northern part of the studied segment (Figs. 1 and 10), the fumarole sample LM (3) and the hot spring sample PM (4) are associated with the Copahue geothermal area, which is set on a “pull apart” like basin, formed by the interplay of the LOFS and the Copahue-Antinir Fault System (CAFS) (Melnick et al., 2006; Fig. 1; Sánchez et al., 2013). A few tens of kilometers towards the south, the occurrence of fumarole sample PL
and Marty, 1995; Hoefs, 2009) and marine limestone (1)

Trajectories for CO₂ loss by calcite precipitation at a temperature of 25 °C are shown in Fig. 6a. The CO₂/3He and δ¹³C-CO₂ plots for the samples are consistent with a volcanic arc signature. The δ¹³C-CO₂ values for the samples range from -6.5 ± 2.2‰ to 6.5 ± 2.2‰, with the highest values observed in the samples from the Pelehue area (8). These samples show a typical volcanic arc signature, with δ¹³C-CO₂ values ranging from -25 to -15‰.

In contrast, the PL (7) sample displays a predominant MORB-like signature, with a δ¹³C-CO₂ value of -15‰. This sample is likely influenced by mixing between MORB and sediments, with almost no contribution from continental crust. The δ¹³C-N values for the samples range from -10‰ to -5‰, indicating that these hot springs have suffered vapor–liquid separation and partial gas-phase loss.

The δ¹³C-N values for the samples from the Pelehue area range from -15‰ to -10‰, suggesting that these hot springs are more easily perceived in such volatile-poor samples. These are among the least contaminated samples in the whole region, with air-corrected ³He/⁴He ratios ranging between 6 and 7.

Further south, in the central part of the studied segment (“b”, Fig. 10), fumaroles and hot springs are spatially associated with stratovolcanoes controlled by transtensional NE-striking faults (e.g., Sollipulli volcano; Fig. 1) or by the intersection between NE- (LOFS) and NW-striking transpressional faults (ALFS) (e.g., Tolhuaca and Cordon Caulle volcanoes; Figs. 1 and 10). These volcanic systems show a higher degree of crustal contamination, with ⁸⁷Sr/⁸⁶Sr ratios higher than lavas related to volcanoes in the northernmost part of the segment (“c”, Fig. 10). The associated thermal manifestations in this area are also characterized by a minor degree of crustal contamination of their magmatic source(s). As shown in Fig. 4, the Rc/Ra ratios in samples JM (9), BB (12), PU (21), AC (22) and RU (23) are among the highest in the region (Rc/Ra ~ 6–7) and correlate with low ⁸⁷Sr/⁸⁶Sr ratios in their host stratovolcanoes. The nitrogen isotope signature suggests mixing between MORB and sediments, with minor contribution from continental crust (Fig. 8). CO₂/³He and δ¹³C-CO₂ show the typical volcanic-arc signature for fumarole sample JM (9), whereas the water-dissolved gas samples are slightly affected by CO₂ loss and δ¹³C-CO₂ fractionation for calcite deposition (Fig. 9).

Finally, the case “c” in Fig. 10 represent all those fumaroles and hot springs associated with stratovolcanoes that are controlled by pure transpressive NW-striking faults (Nevado de Chillan, Villarica and Mocho-Choshuenco volcanoes; Fig. 1, presenting the highest degrees of crustal contamination (NC (1), BT (10), VA (11), RB (13), QC (14), ME (15), PA (16), PF (17), CO (18), TR (19), CH (20)) and the hot springs spatially related with transpressional fault-fracture zones that do not permit a high vertical permeability (TT (2), AV (5), PE (6)).
## Table 3
Volcano-tectonic associations along the studied segment of the SVZ.

<table>
<thead>
<tr>
<th>Group</th>
<th>Name</th>
<th>Location</th>
<th>Description</th>
<th>References</th>
<th>Samples</th>
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<td>a: LOFS northern transtensional termination</td>
<td>Caviahue-Copahue volcanic complex</td>
<td>37° 51'S</td>
<td>The Caviahue-Copahue volcanic complex is located at the northern termination of the LOFS in a “horsetail”-like accommodation zone. The area is limited by two major fault zones, the Copahue–Antinür thrust system to the north and the main branch of the LOFS, to the south, which locally form pull-apart structures. Magmatic products associated with active Copahue volcano vary from basaltic-trachyandesites to trachyandesites. Several NE-striking strike-slip faults and NE-striking half-graben are located within 40 km to the south of the Caviahue-Copahue complex.</td>
<td>Melnick et al. (2006), Varekamp et al. (2006), Rosenau et al. (2006), Pérez-Flores et al. (2014)</td>
<td>LM (3), PM (4)</td>
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<tr>
<td>Pelehue valley</td>
<td>38° 07'S</td>
<td>The area is limited by two major fault zones, the Copahue–Antinür thrust system to the north and the main branch of the LOFS, to the south, which locally form pull-apart structures. Magmatic products associated with active Copahue volcano vary from basaltic-trachyandesites to trachyandesites. Several NE-striking strike-slip faults and NE-striking half-graben are located within 40 km to the south of the Caviahue-Copahue complex.</td>
<td>Melnick et al. (2006), Varekamp et al. (2006), Rosenau et al. (2006), Pérez-Flores et al. (2014)</td>
<td>PL (7), CU (8)</td>
<td></td>
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<tr>
<td>b: LOFS dominant and interplay between LOFS and ALFS</td>
<td>Sollipulli volcano</td>
<td>38° 58’S</td>
<td>Stratovolcanoes and pyroclastic cones that form NE-SW alignments. Mostly basalts have been erupted from these arrays but stratovolcanoes evacuated also dacites or rhyolites</td>
<td>Gilbert et al. (1996); Cembrano and Lara (2009); Lachowycz et al. (2015)</td>
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<td>Antillanca volcanic complex</td>
<td>40° 46’S</td>
<td>Stratovolcanoes or clusters of stratovolcanoes controlled by the interplay of NW-striking sinistral-reverse faults of the ALFS and NE-to NNE-striking dextral-normal faults of LOFS. Volcanic edifices show no asymmetry of the base but they can display flank vents in preferred NW orientation.</td>
<td>Lara et al. (2006), Cembrano and Lara (2009), Pérez-Flores et al. (2014)</td>
<td>JM (9)</td>
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<td>Tolhuaca volcano</td>
<td>38° 19’S</td>
<td>Stratovolcanoes or clusters of stratovolcanoes controlled by the interplay of NW-striking sinistral-reverse faults of the ALFS and NE-to NNE-striking dextral-normal faults of LOFS. Volcanic edifices show no asymmetry of the base but they can display flank vents in preferred NW orientation.</td>
<td>Lara et al. (2006), Cembrano and Lara (2009), Pérez-Flores et al. (2014)</td>
<td>JM (9)</td>
<td></td>
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<tr>
<td>Puyehue-Cordón Caulle volcanic complex</td>
<td>40° 35’S</td>
<td>Stratovolcanoes or clusters of stratovolcanoes controlled by the interplay of NW-striking sinistral-reverse faults of the ALFS and NE-to NNE-striking dextral-normal faults of LOFS. Volcanic edifices show no asymmetry of the base but they can display flank vents in preferred NW orientation.</td>
<td>Lara et al. (2006), Cembrano and Lara (2009), Pérez-Flores et al. (2014)</td>
<td>JM (9)</td>
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<td>c: Dominant ALFS</td>
<td>Nevado de Chillán volcano</td>
<td>36° 52’S</td>
<td>Stratovolcanoes built on top of the NW-striking sinistral-reverse faults from the ALFS. LOFS is represented by the NNE-striking master fault. Volcanic edifices show no or slightly asymmetry of the base and they can display flank vents in NW-preferred orientation. Compositions cover a wide range from basalts to rhyolitic</td>
<td>Melnick et al. (2006), Cembrano and Lara (2009), Sánchez et al. (2013)</td>
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<td>Sierra Nevada volcano</td>
<td>38° 34’S</td>
<td>Stratovolcanoes built on top of the NW-striking sinistral-reverse faults from the ALFS. LOFS is represented by the NNE-striking master fault. Volcanic edifices show no or slightly asymmetry of the base and they can display flank vents in NW-preferred orientation. Compositions cover a wide range from basalts to rhyolitic</td>
<td>Melnick et al. (2006), Cembrano and Lara (2009), Sánchez et al. (2013)</td>
<td>NC (1)</td>
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<td>Villarica-Quetrupillan-Lanín volcanic alignment</td>
<td>39° 25’S – 39° 38’S</td>
<td>Stratovolcanoes built on top of the NW-striking sinistral-reverse faults from the ALFS. LOFS is represented by the NNE-striking master fault. Volcanic edifices show no or slightly asymmetry of the base and they can display flank vents in NW-preferred orientation. Compositions cover a wide range from basalts to rhyolitic</td>
<td>Melnick et al. (2006), Cembrano and Lara (2009), Sánchez et al. (2013)</td>
<td>NC (1)</td>
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<td>Mocho-Choshuenco volcano</td>
<td>39° 56’S</td>
<td>Stratovolcanoes built on top of the NW-striking sinistral-reverse faults from the ALFS. LOFS is represented by the NNE-striking master fault. Volcanic edifices show no or slightly asymmetry of the base and they can display flank vents in NW-preferred orientation. Compositions cover a wide range from basalts to rhyolitic</td>
<td>Melnick et al. (2006), Cembrano and Lara (2009), Sánchez et al. (2013)</td>
<td>NC (1)</td>
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<td>Trapa Trapa thermal spring</td>
<td>37° 41’S</td>
<td>Thermal springs related NW-trending faults of the ALFS. The hot springs are spatially associated with Callaqui stratovolcano, a N60E elongated volcanic fissure, with parasites and pyroclastic cones alignment in the same direction. The composition of erupted products from Callaqui volcano is mainly basaltic-andesitic</td>
<td>Moreno et al. (1984), Potent (2003), Cembrano and Lara (2009), Radic (2010)</td>
<td>TT (2)</td>
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<tr>
<td>Avellano thermal spring</td>
<td>37° 55’S</td>
<td>Thermal springs related NW-trending faults of the ALFS. The hot springs are spatially associated with Callaqui stratovolcano, a N60E elongated volcanic fissure, with parasites and pyroclastic cones alignment in the same direction. The composition of erupted products from Callaqui volcano is mainly basaltic-andesitic</td>
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<td></td>
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<tr>
<td>Pemehue thermal spring</td>
<td>38° 4’S</td>
<td>Thermal springs related NW-trending faults of the ALFS. The hot springs are spatially associated with Callaqui stratovolcano, a N60E elongated volcanic fissure, with parasites and pyroclastic cones alignment in the same direction. The composition of erupted products from Callaqui volcano is mainly basaltic-andesitic</td>
<td>Moreno et al. (1984), Potent (2003), Cembrano and Lara (2009), Radic (2010)</td>
<td>TT (2)</td>
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characterized by a wide range of $^3$He/$^4$He, CO$_2$/$^3$He, $\delta^{13}$C–CO$_2$ and $\delta^{15}$N values. We explain these variations by linking the geochemical data of gas in fumaroles and thermal spring water, to a wider geological context that includes the regional distribution of fault-fracture meshes and the isotopic variation of source magmas.

The first order control on helium, carbon and nitrogen isotopes signatures observed in the studied segment seems to be largely dominated by the degree of crustal assimilation of the magmatic sources, which is in turn controlled by the LOFS and ALFS. As shown in Fig. 4, the air-corrected $^3$He/$^4$He, $\delta^{13}$C–CO$_2$ and $\delta^{15}$N fumarole gas data show a strong correspondence with the $^{87}$Sr/$^{86}$Sr ratios of lavas from hosting volcanic systems. The thermal spring gas data also show a similar correspondence, although partly masked by secondary processes. Our observations also indicate that the magmatic sources of hydrothermal fluids in the region are highly variable at the regional scale, and more primitive signatures are most likely transmitted to the shallow volcanic/geothermal environment along the NNE-striking LOFS.

In contrast, the isotopic signatures of gases in thermal manifestations along the arc-oblique, NW-striking ALFS, show a higher degree of crustal contamination. Considering the fact that the ALFS inhibit vertical fluid permeability due to its misorientation with respect to the prevailing regional stress field, the $^3$He/$^4$He, $\delta^{13}$C–CO$_2$ and $\delta^{15}$N data records crustal contributions related to increased fluid/rock interaction and higher residence times.

Whereas the ALFS promote the formation of long-lived, more evolved high-enthalpy hydrothermal reservoirs (e.g., Toluca geothermal field), the LOFS allow a higher vertical permeability of hydrothermal fluids from more primitive, MORB-like magmatic sources. These large-scale structures are effective loci for enhanced fluid flow, providing a “background” $^3$He/$^4$He signal in the area that exceeds by far the crustal helium signature of 0.05 Ra. This crustal-scale fault system also promote the deep circulation of meteoric fluids, as occurring for thermal springs between 38.5°S and 40°S, that partially masks the deep $\delta^{13}$C–CO$_2$ and $\delta^{15}$N signatures due to shallow processes such as mixing with meteoric water and calcite precipitation.

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REFERENCES


