



Metal Fluxing in a Large-Scale Intra-Arc Fault: Insights from the Liquiñe-Ofqui Fault System in Southern Chile

Daniele Tardani ^{1,2,*}, Martin Reich ^{1,2}, Emilie Roulleau ^{1,2}, Naoto Takahata ³, Yuji Sano ³, José María González-Jiménez ^{1,2}, Pablo Sánchez ^{1,2}, José Cembrano ^{2,4}, Gloria Arancibia ^{2,4}

(1) Department of Geology, Universidad de Chile, Santiago, Chile

(2) Andean Geothermal Center of Excellence (CEGA), Universidad de Chile, Santiago, Chile

(3) Atmosphere and Ocean Research Institute, University of Tokyo, Japan

(4) Dept. of Structural Engineering, Pontificia Universidad Católica de Chile, Santiago, Chile

*Contact email: daniele.tardani@ing.uchile.cl

Abstract. Although it has been recognized that volcanism and hydrothermal activity in the Andean Cordillera of Southern Chile (37–46°S) is controlled by the 1,200 km long NNE-trending Liquiñe-Ofqui Fault System (LOFS), the structural controls on magma degassing and metal fluxing remains poorly constrained. The goal of the study is to test the geological and tectonic controls on the source and transport of volatile components, noble and base metals and metalloids in geothermal fluids from active systems along this segment. For this purpose, we coupled major and trace element concentration data of metals and halogens in geothermal fluids and volcanic fumarole condensates with isotopic ratios of noble gases (He, Ar) and stable isotopes (C, N) in 24 thermal manifestations occurring along extensional and compressional structures of the LOFS. The helium isotopic ratios, defined as R/Ra, range between 2.5 and 7.5 in the studied segment and are indicative of two end-member sources for geothermal fluids. Our data show that high metal concentrations of Fe, As, Zn, Cu and Pd are usually correlated with high vertical permeability, while lower metal concentrations and R/Ra values reflect increased mixing with meteoric water.

Keywords: Trace metals, PGE, R/Ra, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, LOFS

1 Introduction

In the Andean Cordillera of Central-Southern Chile, the nature of the relationship between tectonics and volcanism is the result of interaction between the crustal structures of the basement and the ongoing regional stress field. Between 37° and 46°S, the volcanic and geothermal activity is controlled by the NNE-trending, 1,000 km long Liquiñe-Ofqui Fault System (LOFS) (Cembrano and Lara, 2009). Although there is agreement that volcanism and hydrothermal activity are largely controlled by the regional scale tectonic stress field and the architecture of the volcanic arc, there is still limited information on how the shallower hydrothermal fluids are connected with the deep magmatic sources in this segment. Furthermore, this segment is characterized by a relative paucity of ore deposits over geologic time. Compared with the Andes of north-central Chile (~19–34°S), only a few, small-scale Cu/Au hydrothermal vein deposits (and a few porphyry-Cu prospects) are reported in the studied area of southern Chile (38–40°S).

Between 37–46°S, many geothermal surface manifestation and shallow fumarolic emissions are spatially related to stratovolcanoes and fault segments associated with LOFS (Sánchez et al., 2013). Despite the abundance of regional compilations and studies describing the structural controls on geothermal activity and volcanism (Hilton et al., 1993; Cembrano & Lara, 2009; Ray et al., 2009; Lahsen et al., 2010), is not clear on how the different structural orientations along the LOFS: (1) influence the chemical and isotopic composition of He, C and N, and (2) affect significantly metal transport under variable vertical permeability conditions and degrees of mixing with meteoric water.

In this study we present a comprehensive survey of noble gas (He, Ar) and stable isotope (C, N) data, in thermal springs and fumaroles between 37°S and 41°S. The isotope database is coupled for each thermal manifestation with noble (platinum-group elements and Au) base (Fe, Cu, Zn) metals and metalloids (As, Sb) concentration data. The LOFS is an ideal setting for hypothesis testing, where the high occurrence of fumaroles and thermal springs are related with the NE-SW and NW-SE anisotropies and with the main track of LOFS. In the next sections, we show that these data point to a strong structural control on metal budgets and focused fluid flow in the study region.

2 Background and Methods

Between 37–46°S, basaltic-andesitic magma emplacement is controlled by the 1,000 km long, NNE Liquiñe-Ofqui Fault System (LOFS), an intra-arc transpressional dextral strike-slip fault system, associated with second-order intra-arc anisotropies of overall NE-SW and NW-SE orientation. Cembrano & Lara (2009) have recognized that magmatic evolution in this segment is controlled by these second-order structures, defining (i) kinematically-coupled systems (NE-trending) directly related to the current dextral transpressional tectonic regime, and characterized by primitive magmatic compositions, and (ii) kinematically uncoupled systems (NW-trending), associated with ancient reverse basement faults and showing more evolved compositions. These types of faults have long been recognized to play a key role as host structures and high-permeability flow paths for geothermal systems and

hydrothermal mineralization in Chile and elsewhere (Sibson, 2001; Rowland & Simmons, 2012).

The major cation/anion composition, He, N and C isotopes along with trace metals and metalloids content were measured in 24 selected thermal springs and fumaroles occurring along the LOFS and associated second-order faults (Fig.1). Fumarole condensates and thermal spring waters were collected in pre cleaned, high-density polythene bottles. Thermal waters were filtered using 0.45 μm membrane filters and acidified using HNO_3 4N. Major cations and anions were determined using a combination of ion chromatography (IC) and atomic absorption spectrometry (AAS) at the Andean Geothermal Center of Excellence (CEGA) Laboratories, Universidad de Chile. Trace metals contents were analyzed in ACTLABS laboratories using HR-ICP-MS techniques. In addition to the concentration data, fumarole and thermal water samples were collected in Pb glass bottles and analyzed for He, Ar, N, C and S isotopes at the AORI Institute at the University of Tokyo in Japan.

3 Results

3.1 Helium isotopes ratios

Helium isotopes results are expressed as R_c/R_a [$(^3\text{He}/^4\text{He}_{\text{sample}})/(^3\text{He}/^4\text{He}_{\text{air}})$], and were corrected for air contamination using the $^{20}\text{Ne}/^4\text{He}$ ratio (Marty et al., 1989, Sano et al., 2013). The R_c/R_a ratios and its distribution along the fault are shown in Figure 1. The highest R_c/R_a ratios (>7) were found in fumaroles samples from the Pelehue and Copahue geothermal areas, located in the north-eastern part of LOFS. High R_c/R_a ratios (>6) were also measured in thermal spring samples from Pucon Mahuida, Coyuco and in fumarole samples from the Tolhuaca volcano in the northern termination of the LOFS. Also, high $R_c/R_a > 6$ values were measured in water samples from the Balboa springs near Solipulli, and in bubbling gas samples from Termas de Aguas Calientes, Termas de Puyehue and Baños de Rupanco.

Mid R_c/R_a values (4-6) were observed in spring water samples along most of the studied LOFS segment. Finally, the lowest R_c/R_a ratios (<4) were measured in fumarole gas samples from the Nevados de Chillán volcano and in water samples near the Villarica volcano, where several thermal springs are located on the main track of LOFS.

3.2 Stable isotopes of carbon and nitrogen

The $\delta^{15}\text{N}$ values of thermal spring samples and fumaroles range between $-3.01 \pm 0.2\%$ (2σ) and $4.93 \pm 0.2\%$ (2σ), within the accepted range for subduction settings (-6% to $+6\%$; Fischer et al., 2002; Hilton et al., 2002). The $\delta^{13}\text{C}-\text{CO}_2$ values range from $-30.72 \pm 0.28\%$ (2σ) to -7.44 ± 0.14 (2σ), covering the entire observed range of high temperature

volcanic gases in subduction zones, i.e., from MORB (-6.5%) to sediments (-30%) (Sano and Marty, 1995).

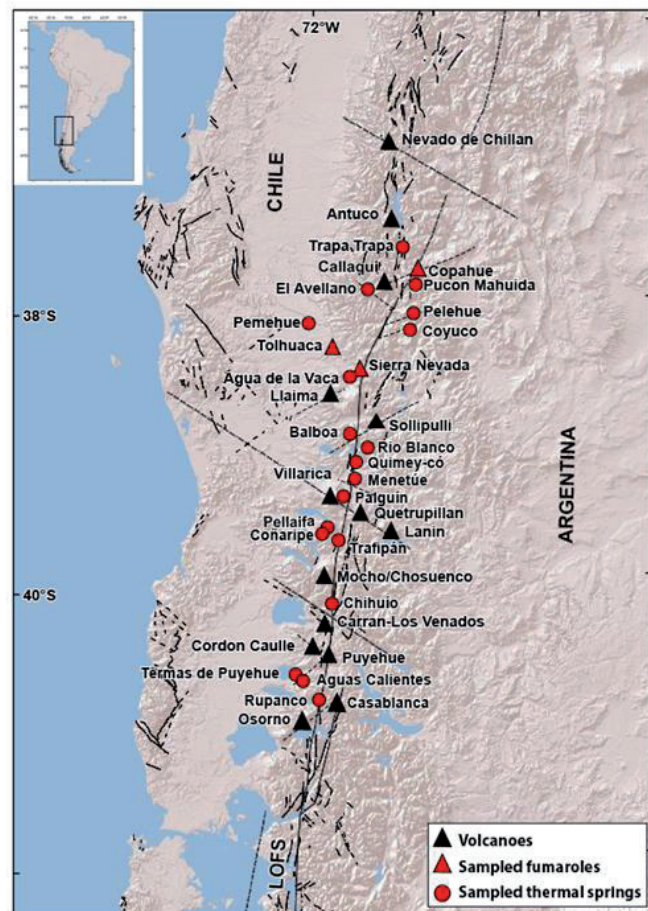


Figure 1. Location of sampled fumaroles and thermal springs along the LOFS and secondary structures. Faults distribution was taken from Cembrano & Lara (2009), Lara et al (2006) and Potent (2001).

3.3 Trace elements concentrations

The concentration of 61 trace elements were obtained in water and fumarole condensates, revealing anomalously high concentrations of base metals (Fe, Cu, Zn), metalloids (As, Sb) and PGEs (Pd, Rh). Base metals concentrations range from 1 ppb up to 370 ppm for Fe, 0.06 to 4.78 ppb for Cu and 2 to 210 ppb for Zn. Arsenic and Sb concentrations are between 3-4000 ppb and 0.01-17.00 ppb, respectively. Measured values of PGE are unusually high for shallow, low-temperature, thermal spring waters. The amounts of Pd range between 0.01 and 2.00 ppb and between 0.001 and 0.150 ppb for Rh. Similar concentrations have been reported in thermal fluids from Salton Sea, in deep geothermal fluids (McKibben & Williams, 1990) and in mud pots in Mutnovsky volcano in South Kamchatka (Bortnikova et al., 2008).

4 Discussions

4.1 Origin of fluids in the LOFS

In general terms, the He, N, and C isotopic ratios of fumaroles and thermal waters show no systematic longitudinal or latitudinal variations. Thermal fluids from the LOFS result from mixing between a three-source component system, i.e., Mantle, Crust and Air Saturated Water (ASW). Based on this, it is possible to discriminate at least three groups of samples with variable degrees of mixing. The most primitive signature (M 100%) was identified at Copahue and Pelehue, situated in the northernmost part of the study area, where the LOFS bends eastward and decomposes into a series of NNW- to NE-striking extensional and transtensional fault splays that form an arrangement with a horsetail-like geometry (Rosenau et al., 2006).

These structures, due to their high permeability, promote vertical fluid circulation (Rowland and Simmons, 2012), minimizing the reaction between fluids and crust.

A relatively lower degree of crustal contamination (M 80-90%) was found in thermal springs or fumaroles associated with NE-trending structures, as identified by Cembrano & Lara (2009). These correspond to high vertical permeability zones within the main fault. Finally, the highest degrees of crustal contamination (M<60%) were found in thermal springs located along the main trace of the LOFS, and along the arc-oblique NW-trending structures.

The nitrogen isotope composition of fumaroles and thermal springs ($\delta^{15}\text{N}$) have been interpreted how a mixing between deep nitrogen source (i.e., sediment recycled from the subducted plate) and a shallow air saturated water. The higher $\delta^{15}\text{N}$ ratios were observed in both the northern termination of the LOFS (37-38°S) and in the south portion of the studied area (i.e., Termas de Aguas Calientes, near the Puyehue volcano). In contrast, all thermal springs between 39-40°S and located on the main trace on the LOFS have $\delta^{15}\text{N}$ near air value. These results are indicative of structurally-controlled mixing of deep magmatic fluids with shallow waters of meteoric origin

4.2 Sources of metals

As already mentioned above, thermal springs and fumaroles along the LOFS have relatively high trace metals contents. Results show two different trends for selected metals that may reflect two different sources. First, we observed a broad correspondence of Cu and Pd with $^4\text{He}/^{20}\text{Ne}$ ratios. This suggests that metal enrichment may occur in geothermal systems with lower degrees of mixing between deep hydrothermal fluids and meteoric water.

In contrast, metalloids (As, Sb, B) as well as Li, Cs, Rb and Sr, show a broad decreasing trend with $^4\text{He}/^{20}\text{Ne}$ ratios. These results are indicative of participation of a crustal source of magmatic vapor.

5 Conclusions

In order to explore the feedbacks between structures, fluid sources and metal transport, we evaluated the differences of He, N and C isotopic ratios in shallow thermal emissions located along the LOFS and its associated structures. What found a marked difference in the He isotope signature of thermal manifestations that are affected by high vs. low vertical permeability structures.

Furthermore, the trace metal content of thermal fluids is apparently not affected by variable degrees of mantle-crust interaction, but rather by mixing between deep hydrothermal fluids (possibly enriched in metals) and meteoric water.

Acknowledgements

Financial support for this study was provided by FONDECYT N°1130030 and by FONDAP project 15090013, “CEGA”. Further support was provided by ICM grant NC130065 “Millennium Nucleus for Metal Tracing Along Subduction”. Daniele Tardani thanks MECESUP for providing support through a Ph.D. scholarship.

References

- Bortnikova S.B., Bessonova E.P., Gavrilenko G.M., Vernikovskaya I.V., Bortnikova S.P., Palchik N.A. 2008. Hydrogeochemistry of thermal sources, Mutnovsky volcano, South Kamchatka (Russia). Thirty-Third Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, January 28-30, 2008.
- Cembrano, J., Lara, L. (2009). The link between volcanism and tectonics in the southern volcanic zone of the Chilean Andes: A review. *Tectonophysics* 471, 96–113.
- Fischer, T.P., Hilton, D.R., Zimmer, M.M., Shaw, A.M., Sharp, Z.D., Walker, J.A., 2002. Subduction and recycling of nitrogen along the Central American margin. *Science* 297, 1154–1157.
- Hilton D.R., Hammerschmidt K., Teufel S., Friedrichsen H. 1993. Helium isotopes characteristics of Andean geothermal fluids and lavas. *Earth and Planetary Science Letters* 120 (1993) 265-282.
- Hilton, D.R., Fischer, T.P., Marty, B., 2002. Noble gases and volatile recycling at subduction zones. In: Porcelli, D.P., Ballentine, C.J., Wieler, R. (Eds.), *Reviews in Mineralogy and Geochemistry: Noble Gases in Geochemistry and Cosmochemistry*, vol. 47, pp. 319–370.
- Lahsen, A., Muñoz, N., Parada, M.A. (2010). Geothermal development in Chile. *Proceedings World Geothermal Congress, Bali, Indonesia, Paper N° 25*.
- Lara, L.E., Lavenu, A., Cembrano, J., Rodríguez, C., 2006a. Structural controls of volcanism in transversal chains: resheared faults and neotectonics in the Cordón Caulle–Puyehue area (40.5°S), Southern Andes. *Journal of Volcanology and Geothermal Research* 158, 70–86

- Marty, B., Jambon, A., Sano, Y., 1989. Helium isotopes and CO₂ in volcanic gases of Japan. *Chemical Geology* 76, 25–40
- McKibben M.A. & Williams A.E., 1990. Solubility and transport of platinum group elements and Au in saline hydrothermal fluids: constraints from geothermal brine data. *Economic Geology*, Vol. 85, 1990, pp. 1926-1934.
- Potent, S., Reuther, C.D., 2001. Neogene Deformationsprozesse im aktiven magmatischen Bogen Südzentralchiles zwischen 37 und 39°S. *Mitteilungen Geologisch-Paläontologisches Institut Universität Hamburg* 85, 1–22.
- Ray M.C., Hilton D.R., Muñoz J., Fischer T., Shaw A.M. 2009. The effects of volatile recycling, degassing and crustal contamination on the helium and carbon geochemistry of hydrothermal fluids from the Southern Volcanic Zone of Chile. *Chemical Geology* 266 (2009) 38–49.
- Rosenau, M., Melnick, D., Echtler, H. (2006) Kinematic constraints on intra-arc shear and strain partitioning in the southern Andes between 38°S and 42°S latitude. *Tectonics* 25, TC4013.
- Rowland, J.V., and Simmons, S.F. (2012) Hydrologic, Magmatic, and Tectonic Controls on Hydrothermal Flow, Taupo Volcanic Zone, New Zealand: Implications for the Formation of Epithermal Vein Deposits. *Econ. Geol.* 107, 427-457.
- Sánchez, P., Pérez-Flores, P., Arancibia, G., Cembrano, J., Reich, M. 2013. Crustal deformation effect on the chemical evolution of geothermal systems: the intra-arc Liquiñe-Ofqui fault system, Southern Andes. *International Geology Review*, 2013 <http://dx.doi.org/10.1080/00206814.2013.775731>
- Sano, Y., Marty, B., 1995. Origin of carbon in fumarolic gas from island arcs. *Chemical Geology* 119, 265–274
- Sano, Y., Marty, B., Burnard, P., 2013. Noble gases in the atmosphere. In: Burnard, P. (Ed.). *The Noble Gases as Geochemical Tracers, Advances in Isotope Geochemistry*. Springer-Verlag, Berlin Heidelberg, pp. 17–31.
- Sibson, R.H. (2001) Seismogenic framework for hydrothermal transport and ore deposition. *Rev. Econ. Geol.* 14, 25-50.