Manuscript Number:

Title: Petrological and noble-gas features of Lascar and Lastarria volcanoes (Chile): inferences on plumbing systems and mantle characteristics

Article Type: Regular Article

Keywords: Lascar; Lastarria; Noble Gases; Fluid inclusions; Mantle

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Abstract: Lascar (5,592 m a.s.l.) and Lastarria (5,697 m a.s.l.) are Chilean stratovolcanoes located in the Central Volcanic Zone (16°S to 28°S) that have developed over-71 km of continental crust. Independently of the similarities in their Plinian/Vulcanian eruptive styles, their complex magmatic feeding structures and the origins of their magmatic fluids still necessitate constraints in order to improve the reliability of geochemical monitoring. Here we investigate the petrography, bulk-rock chemistry, and mineral chemistry in products from the 1989-1993 explosive eruptive cycle at Lascar and from several Holocene eruptive sequences at Lastarria. These data are integrated with measurements of the noble-gas isotopes in fluid inclusions of minerals from the same products as well as in fumarole gases. Petrography, bulk-rock chemistry, and mineral chemistry show that the studied rocks belong to high-K-calc-alkaline series and provide evidence of differentiation, mixing, and crustal assimilation. The deepest crystallization processes occurred at variable levels of the plumbing systems according to the lithostatic equivalent depths estimated with mineral equilibrium geobarometers at Lascar (15-29 km) and Lastarria (~20-40 km). The 40Ar/36Ar and 4He/20Ne ratios indicate the presence of some degree of air contamination in the fluids from both volcanoes. The 3He/4He values at Lascar (6.91-7.12 Ra) are relatively homogeneous and comparable to those of fumaroles, suggesting a main zone of magma crystallization and degassing. In contrast, the 3He/4He values at Lastarria (5.31-8.01 Ra) vary over a wide range, suggesting various magma storage levels and providing evidence of crustal contamination, as indicated by the rock chemistry. We argue that mantle beneath the two volcanoes could have slight differences induced by distinct subducting rocks and conditions. However, we cannot exclude that crustal contamination contributes to the different measured signatures.

Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given: Data will be made available on request





Dr X-H Li Editor in-chef Lithos

Santiago, December 24 2019

Dear Dr Li,

Please find here, our manuscript: "Petrological and noble-gas features of Lascar and Lastarria volcanoes (Chile): inferences on plumbing systems and mantle characteristics ", authors: Robidoux, P., Rizzo, A.L., Aguilera F., Aiuppa A., Artale M., Liuzzo M., Nazzari M., Zummo F.", which we submit for your consideration as an article for Lithos.

We report here on the first direct measurements of noble gas (He-Ne-Ar) isotopic compositions in fluid inclusions in olivine and pyroxene crystals at Lascar and Lastarria volcano, Chile. The magmas produced by both stratovolcanoes, since Holocene, represent MORB-like and volcanic arc signatures contaminated by crust according to bulk rock chemistry. Most important, during the last decades, Lascar still hold noble gas values coinciding with fluids trapped in fluid inclusions from mafic minerals sampled in eruptive material from the 1989-1993's period of activity. In comparison, Lastarria volcano show primitive MORB values in Holocene products, but large heterogeneities on dataset rather may represent cortical and atmospheric contamination on ascending magma through a complex plumbing system with different ponding zones below the Andean Cordillera.

Our results contribute to a better understanding of the mantle fluid chemistry from magmas that travel in plumbing system form typical active stratovolcanoes in Northern Chile, and allow refining a novel petrological method to discriminate fluid sources from fumaroles at monitored volcanoes.

For the reasons above, we believe our study would attract the attention of a variety of earth scientists interested by petrological processes in active volcanoes, from matnle-to-lithospheric conditions. Given the inherent practical contribution of the investigation for volcanic risks and applied petrology, we believe that Lithos would make a perfect output for our manuscript.

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Yours Sincerely Philippe Robidoux

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Highlights

- Lascar noble gases in fumaroles coincident with trapped fluids in crystals
- Bulk rock and crystal chemistry at Lastarria reflect larger magma residence times
- Deepest polybaric crystal fractioning conditions at Lascar and Lastarria at 40 km
- Subducting magmas with MORB and volcanic arc signatures contaminated by crust

Petrological and noble-gas features of Lascar and Lastarria volcanoes

- 3 (Chile): inferences on plumbing systems and mantle characteristics
- 4
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- 25

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 conditions. However, we cannot exclude that crustal contamination contributes to
 the different measured signatures.

53

54 **1. Introduction**

Lascar and Lastarria (Chile) are two of the most actively degassing quiescent 55 stratovolcanoes in the Central Volcanic Zone (CVZ) (Tamburello et al., 2015), 56 and they have a long record of volcanic eruptions with magnitudes up to 57 58 Plinian/Vulcanian. Lascar erupted frequently during the Holocene, and a recent short-lived magmatic intrusive event was responsible for major explosive 59 eruptions in 1993 (Matthews et al., 1994; Gardeweg et al., 1998, 2011; Calder et 60 al., 2000). Lastarria has exhibited major explosive eruptions separated by longer 61 time intervals compared with those at Lascar (Aguilera, 2008; Naranjo, 2010). 62

The available petrological and geophysical information indicates that the 63 two volcanoes have complex plumbing systems and different magma residence 64 times in crustal reservoirs (Naranjo, 2010; Aguilera et al., 2012). For example, 65 the 1993 eruptive products are thought to have erupted from the superficial 66 (~2 km deep) magma ponding zone at Lascar, although mineral-melt equilibria 67 imply a vertically elongated plumbing system extending as deep as 11.5 km (up 68 69 to ~500 MPa; Stechern et al., 2017). Seismic tomography has indicated that magma could actually be stored from as shallow as ~1 km to as deep as 5-6 km 70 71 at Lastarria (Spica et al., 2015).

72 Despite numerous studies, the complex magmatic feeding systems and the origin of magmatic volatiles remain only partially understood at both volcanoes. In 73 addition, despite the volcanoes being located at the edge of the Andean 74 subduction zone above ~71 km of rigid continental crust (Thorpe et al., 1982), the 75 impact of crustal assimilation on the composition of intruding magma is poorly 76 77 understood. It remains unclear whether the magmatic fluids that today feed fumarole emissions originate from fresh and undegassed newly ascending 78 magma or from more-aged stored melts. 79

80 In this work we combine petrological data with noble-gas analyses of fluid inclusions (FIs) in olivines and clinopyroxenes (Cpx) to address some of the 81 above open questions. We report on the major-element chemistry of the mineral 82 assemblage integrated with analyses of bulk-rock major and trace elements to 83 characterize the mantle contribution of magma and levels of magma storage 84 below Lascar and Lastarria volcanoes. We also attempt to identify possible 85 differences between the two plumbing systems, and the role of continental crust 86 in contaminating magma compositions. FI noble-gas isotope signatures are 87 88 compared with new information and that in the literature on the fumaroles to assess shallow atmospheric contamination, and mantle versus crustal origins of 89 volatiles in the shallow plumbing systems. 90

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2. Geological and geodynamic setting

Orogenic andesitic stratovolcanoes from the Neogene to the present day along
the South American Volcanic Arc are structurally and compositionally grouped in

three main zones from north to south: (1) Northern Volcanic Zone (5°N to 2°S), 95 (2) CVZ (16°S to 28°S), and (3) Southern Volcanic Zone (33°S to 52°S) (Thorpe 96 and Francis, 1979; Thorpe et al., 1982; Harmon et al., 1984). From north to south 97 the crust thickness varies between 30 and 71 km. The variable depth of the 98 Benioff plan (80–120 km) plays a major role in delivering slab fluid and the partial 99 melting of the mantle wedge, while crustal assimilation impacts the K content of 100 the magma (Stern, 2004), contributing to defining calc-alkaline (CA) versus 101 shoshonitic volcanic rock series (Stern, 2004). The convergence rate averages 102 7 cm/year (DeMets et al., 2010) and trench structures vary from deep, dry, and 103 sediment-poor in the north, to shallow and sediment-rich in the south (Völker et 104 al., 2013). 105

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107 **2.1 Chemistry of CVZ magmas**

Magmas in the Andean CVZ are mainly andesites to dacites, but some mafic and 108 felsic endmember magmas have also been found (Wörner et al., 2018 and 109 references therein). The continental crust contamination is greater in CVZ 110 magmas than in the rest of the South American Volcanic Arc, as testified by their 111 higher ⁸⁷Sr/⁸⁶Sr, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb ratios, and lower ¹⁴³Nd/¹⁴⁴Nd ratios 112 (e.g. Harmon et al., 1984; Thorpe et al., 1984; Hickey et al., 1986; Hildreth and 113 114 Moorbath, 1988; de Silva, 1991; Davidson and de Silva, 1992; Wörner et al., 1994; Haschke et al., 2006; Mamani et al., 2008, 2010; Jacques et al., 2014; Kay 115 et al., 2014; Scott et al., 2018; Wörner et al., 2018). Overall the Sr and Pb isotope 116 117 concentrations decrease (and the Nd concentrations increase) with the age of rocks, except for the majority of the Mesozoic volcanic fields and ignimbrites thatinclude evolved endmembers (de Silva et al., 2006).

The patterns of rare earth elements (REE) are typical of volcanic arc settings, but indicate frequent heterogeneities with N-MORB, E-MORB, and OIB signatures due to large variations in different accreted terrains (Mamani et al., 2008, 2010 and references therein).

- 124
- 125 2.1.1 Lascar volcano

Lascar volcano (23.37°S and 67.73°W, 5,592 m a.s.l.) is a stratovolcano located 126 in the central part of the CVZ (Fig. 1). This volcano comprises two cones hosting 127 five nested craters trending along an ENE-WSW direction. The central crater is 128 the currently active vent and is characterized by intense fumarole activity. 129 Records of eruptive activity date back to the 19th century and cover more than 40 130 eruptions (e.g., Aquilera, 2004 and references therein). The activity was most 131 intense between 1984 and 1994, when three main dome growth-and-collapse 132 cycles generated lava domes that were successively destroyed by moderate 133 Vulcanian eruptions (Matthews et al., 1997). 134

The most-prominent event recorded in historical time was the 1993 sub-Plinian eruptive phase. The eruption emitted 0.1 km³ of rocks, generating eruptive columns that reached up to 25 km, pyroclastic flows going down the NW and SE flanks extending as far as 8 km from the active crater (Gardeweg and Medina, 1994), and falls of tephra that were detected in Argentina, Paraguay, Brazil, and Uruguay (BGVN, 1994). The last explosion was recorded on October 30, 2015, whose eruptive column reached 2.5 km above the active crater (BGVN,
2016). A permanent gas plume is emitted from the active crater, where highly
variable SO₂ fluxes have been recorded during 1989–2011, ranging between 150
and 2,300 tons/day (e.g., Andres et al., 1998; Menard et al., 2014).

According to Gardeweg et al. (1998, 2011), Lascar volcano is built over a basement constituted by volcanic/volcaniclastic/sedimentary basements and granitoids rocks from Permian to Miocene. Upper Miocene to Pleistocene strata of large ignimbrite, domes, and volcanic rocks follow the sequence. Gardeweg et al. (2011) divided the evolution of Lascar volcano over the basement into four stages ranging from ca. 240 ky up to the present day (Gardeweg et al., 1998; Calder et al., 2000).

The eruptive products emitted from Lascar volcano belong to moderate-tohigh K-CA series. Their 86 Sr/ 87 Sr isotope ratios and ϵ Nd values suggest a moderate crustal contamination (Matthews et al., 1994). The major- and traceelement chemistry revealed by rock analyses suggests that fractional crystallization and magma mixing are the key petrogenetic processes (Matthews et al., 1994).

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159 **2.1.2 Lastarria volcano**

Lastarria volcano (also called Lastarria sensu stricto; 25.16°S and 68.50°W, 5,697 m a.s.l.) is a composite stratovolcano located in the southern part of the CVZ (Fig. 1). It forms part of a major volcanic structure called the Lastarria Volcanic Complex (LVC), which also includes the Southern Spur volcano and Negriales lava field (Naranjo, 2010). Lastarria is a single edifice (~10 km³) constituted by five nested craters that are aligned along a north–south direction. Four permanent fumarole fields are currently located along the rim of crater 4, inside crater 5, and on its northwestern flank, each covering 0.001–0.04 km² and characterized by intense fumarole activity (Fig. 1b; Aguilera, 2008).

Lastarria volcano has undergone ground deformation and been 169 characterized by a long period of earthquakes since at least 1997 (Pritchard and 170 Simons, 2004; Froger et al., 2007). A major deformation is centered on the so-171 called Lazufre area (constituting the LVC, Cordón del Azufre, and Bayo 172 volcanoes), with a depth of 7–15 km and a deformation rate of 2–3 cm/year, with 173 some areas related to an overpressure source (e.g., boiling aguifer) lying 174 1,000 m below the crater area (Pritchard and Simons, 2002; Froger et al., 2007; 175 Ruch et al., 2009; Budach et al., 2013; Spica et al., 2015; Díaz et al., 2015). 176

The LVC has formed over Upper Miocene/Upper Pleistocene volcanic rocks corresponding to andesitic-to-dacitic lava flows and domes, with subordinate basaltic andesite lava flows (Naranjo, 1992, 2010). Pyroclastic rocks corresponding to Lower Pleistocene dacitic ignimbrites are also present.

Naranjo (2010) summarized the geological evolution of the LVC into three major volcanic structures: (1) Negriales lava field (400±60 to 116±26 ky [mean±SD]; Middle to Upper Pleistocene), (2) Espolón Sur (Southern Spur) (150±50 ky; Middle Pleistocene), and (3) Lastarria sensu stricto. Naranjo divided the evolution of the LVC into 10 stages ranging from 330±100 to 249±36 ky (Middle Pleistocene) up to the Holocene and present day. The eruptive products from Lastarria volcano belong to high-K calc-alkaline (HK-CA) series (Mamani et al., 2008, 2010; Naranjo, 2010). The compositions of Sr, Nd, and Pb isotopes (Trumbull et al., 1999; Mamani et al., 2008, 2010) suggest high levels of crustal contamination due to a thick continental crust (Trumbull et al., 1999).

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- **3. Sampling and methods**
- **3.1 Sampling locations**

195 **3.1.1 Rocks**

The Lascar rock samples LAS1, LAS2, and LAS3 are crystal-rich scoriae 196 from pyroclastic-flow deposits emitted from the central crater (Table 1). The 197 youngest material collected was emitted during the sub-Plinian eruption in April 198 18–21, 1993 (Gardeweg et al., 1993; Matthews et al., 1994; Sparks et al., 1997; 199 Calder et al., 2000). Distant pyroclastic deposits located on the northwestern 200 flank were found to be abundant in white pumices (Matthews et al., 1994) and 201 dark-color clasts of large scoria bombs and crystalline blocks (up to 1 m). The 202 white and vesicular pumices (described and studied by Matthews et al., 1994; 203 Sparks et al., 1997; Calder et al., 2000) were not collected because they are not 204 associated with the mafic juvenile source and do not contain large quantities of 205 206 visible olivines and pyroxenes. Our sampling thus preferentially targeted the dark scoria with sizes ranging from lapilli to bombs and gray block fragments of the 207 pyroclastic-flow deposits. More specifically, we present data for the crystalline 208

porphyric dome fragments emitted during 1989-1990 (LAS1) and juvenile scoria
(LAS2) (Matthews et al., 1994).

We also studied the Tumbres scoriaceous pyroclastic flow (ca. 9.2 ky; Gardeweg et al., 2011) sampled in outcrops in the southern Tumbres area and in the Talabre Viejo canyon. This sampling site corresponds to the northeastern border of the flow, and several fragments weighing >3 kg were taken from large scoria bombs (LAS3). Textures were similar to LAS2 scoriae, but the LAS3 scoriae presented alternating gray and beige surfaces. Full details on the locations of the deposits are presented in Table 1.

Sampling at Lastarria was performed on the northwestern flank and 218 concentrated on Holocene pyroclastic-flow deposits containing scoriaceous lapilli 219 and bombs, banded black and beige pumices, and lithic block components 220 (Table 1; Naranjo, 2010). LRA1 and LRA2 are scoria fragments with sizes 221 ranging from lapilli to bombs that fall under the "grey IV pyroclastic flow deposit" 222 definition reported by Naranjo (1992), later renamed as "Ignimbrite 3" by Naranjo 223 (2010) (Table 1 provides a list of equivalent names). This flow was emitted by 224 225 crater 4, where most of the actual summit fumaroles are located (Aguilera, 2008). The pyroclastic deposit is dated 2.46±0.04 ky A.P. (Naranjo, 2010). The LRA3 226 sample consists of crystalline pumice fragments from the ~2.5-4.8 ky (~late 227 228 Holocene) Ignimbrite 2 of Naranjo (2010), corresponding to the "grey I pyroclastic flow deposit" defined by Naranjo (1985, 1992). The LRA4 rock samples are pale 229 crystalline pumice fragments emitted by crater 3, which is older. From the 230 231 position of the sampling site, petrographic features, and stratigraphic position (the fragments are white pumices covering the superior layer of the flow margin), we infer that LRA4 is associated with the 4.85±0.04 ky A.P. Ignimbrite 1 described in Naranjo (2010), and more specifically with the "pink pyroclastic flow deposit" defined by Naranjo (1992).

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237 3.1.2 Gases

Fumarole gas samples were collected on the northwestern flank of Lastarria 238 during the 2014 IAVCEI CCVG (Commission on Chemistry of Volcanic Gases) 239 12th Volcanic Gas Workshop (Lopez et al., 2018). Gas was sampled using a 240 titanium tube inserted into the fumarole soil, then connected to a guartz line, with 241 a silicone tube equipped with a three-way valve connected to a syringe for 242 pumping the gas. Dry gases were finally stored in glass bottles for subsequent 243 laboratory analyses. Further details of the study protocol can be found in Lopez 244 et al. (2018). 245

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247 **3.2 Analytical techniques**

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3.2.1 Bulk-rock major and trace elements

Rock samples were prepared for analyzing major and trace elements in the DiSTeM laboratory at the University of Palermo. Bulk-rock analyses were performed at Activation Laboratories (Ancaster, Canada) following techniques described in i.e. Di Piazza et al. (2015) and Robidoux et al. (2017).

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3.2.2 Mineral and glass chemistry

The mineral chemistry of the FI-hosted minerals was studied using electron 256 microprobe analysis (EMPA). For this purpose, sampled blocks, scoria, and 257 pumice fragments containing phenocrysts (Tables 1 and 2) were crushed and 258 sieved several times until a homogeneous grain size of 0.5-1.0 mm was 259 obtained. Several number of phenocrysts in this granulometric size range at 260 Lascar (n=163) and Lastarria (n=138) were then characterized. Dense 261 phenocrysts (>2.63 g/cm³) were separated from scoria, and less-dense minerals 262 (e.g., plagioclase) were separated using sodium polytungstate liquid columns. 263 The separated minerals were collected and washed with deionized water and 264 acetone. The remaining scoria and plagioclase samples were also stored and 265 washed. 266

267 Mineral chemistry was analyzed at the HPHT (high-pressure/high-268 | temperature) laboratory

of Istituto Nazionale di Geofisica e Vulcanologia (INGV) in Rome using an 269 electron microprobe analyzer (JXA-8200, JEOL) equipped with five wavelength-270 dispersive X-ray spectrometers and one energy-dispersive X-ray spectrometer 271 analyzer. Plagioclases, olivines, Cpx/orthopyroxenes (Opx), and biotites were all 272 prepared on different mounts after using abrasives and polishing down to 6-, 3-, 273 274 and 1-µm diamond powder fractions. A set of reference crystals was used for quantifying major elements (the measurement uncertainties are described in 275 Appendix I). At least two spots on both the core and rim of each crystal were 276 277 analyzed to identify composition changes during crystal growth (Appendixes I–V).

Matrix glass on the rim of separated phenocrysts and background (matrix) glass obtained from prepared thin sections were probed by EMPA. Glass surfaces from phenocrysts and closed inclusions with glassy texture were selected to study the chemical equilibrium in liquid–mineral and Opx–Cpx associations. The EMPA conditions were a beam current of 7.50 nA, accelerating voltage of 15 kV, and beam diameter of 5 μ m. The counting times for the minerals were 10 and 5 s at the peak and background, respectively.

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286 **3.2.3 Noble-gas element and isotope compositions**

287 3.2.3.1 Fumaroles

The concentrations and isotope compositions of noble gases (He and Ne) 288 in fumarole gases were determined at the INGV laboratories in Palermo. The 289 ³He, ⁴He, and ²⁰Ne concentrations were measured separately in a split-flight-tube 290 mass spectrometer (GVI-Helix SFT, for analyzing the He isotopes) and in a 291 multicollector mass spectrometer (Thermo-Helix MC Plus, for analyzing ²⁰Ne) 292 after applying standard purification procedures (Di Piazza et al., 2015; Rizzo et 293 al., 2015, 2016). The ³He/⁴He ratio was expressed in units of R/Ra (where Ra is 294 the He-isotope ratio of air, 1.39×10^{-6}), and the analytical uncertainty (1 σ) in single 295 measurements was generally <0.3% (Table 3). The used standard was air, 296 whose reproducibility across >50 analyses performed over several months was 297 <3%. The ³He/⁴He ratios were corrected for atmospheric contamination using the 298 measured ⁴He/²⁰Ne ratio (e.g., Sano and Wakita, 1985; Rizzo et al., 2015) as 299 follows: 300

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where subscripts M and A refer to measured and atmospheric values, respectively [(He/Ne)_A=0.318]. The corrected 3 He/ 4 He ratios are reported in the main text and Table 3 as Rc/Ra values. The correction is small or negligible for most of the samples, with the maximum bias of ~0.2 Ra appearing in the sample showing the lowest 4 He/ 20 Ne value.

The Ar concentrations and isotope compositions (36 Ar, 38 Ar, and 40 Ar) were quantified in a multicollector mass spectrometer (Helix MC-GVI). The analytical uncertainty (1 σ) for single 40 Ar/ 36 Ar measurements was <0.1%. The used standard was air, whose reproducibility over 1 year of daily analyses was <3.5%. Typical blanks for He, Ne, and Ar were <10⁻¹⁵, <10⁻¹⁶, and <10⁻¹⁴ mol, respectively, and are at least two orders of magnitude lower than the sample signals.

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3.2.3.1 Fls in olivine and pyroxene crystals

The element and isotope compositions of He, Ne, and Ar were measured in Fls hosted in the olivine and pyroxene crystals at the INGV laboratories in Palermo (Table 4). Fluids are trapped as spherical or ellipsoidal gas or liquid bubbles during and after magma crystallization (Roedder, 1979, 1984). The olivine and pyroxene crystals were separated from fractions with sizes of 0.5–1 mm. The selected crystals were then cleaned and prepared for noble-gas measurements in accordance with a reproductible protocol (i.e. consult Di Piazza et al., 2015; Rizzo et al., 2015; Robidoux et al., 2017; Battaglia et al., 2018). Each group of samples (0.1–1.3 g) was then loaded into a six-position stainless-steel crusher. Noble gases trapped inside the FIs were released after in-vacuo single-step crushing, which minimizes the contribution of cosmogenic ³He and radiogenic ⁴He that could be trapped in the crystal lattice (e.g., Hilton et al., 2002; Rizzo et al., 2015).

He isotopes (³He and ⁴He) and ²⁰Ne were measured separately by two different split-flight-tube mass spectrometers (Helix SFT-Thermo). The analytical uncertainty (1 σ) of the He-isotope ratio measurements was <5%. The used standard was air, whose reproducibility across >20 analyses performed over several months was <2%.

Ar isotopes (36 Ar, 38 Ar, and 40 Ar) were analyzed by a multicollector mass spectrometer (GVI Argus) at an analytical uncertainty (1 σ) of <0.4%. The used standard was air, whose reproducibility across analyses performed over >2 years was <1%.

Typical blanks for He, Ne, and Ar were $<10^{-14}$, $<10^{-16}$ and $<10^{-14}$ mol, respectively, and were at least one order of magnitude lower than the values measured in the samples. Further details about the sample preparation and analytical procedures are available in Di Piazza et al. (2015), Rizzo et al. (2015), Robidoux et al. (2017), and Battaglia et al. (2018).

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347 **4 Results**

348 4.1 Bulk-rock geochemistry

349 **4.1.1 Lascar volcano**

The major-element compositions of bulk-rock samples are presented in Table 2. 350 Our Lascar rock samples are andesitic (Fig. 2a) and fairly homogeneous 351 $(SiO_2=58.1-58.3 \text{ wt\%}, K_2O=1.56-1.62 \text{ wt\%})$, and thus overlap with the 352 compositions of the least-differentiated Lascar mafic enclaves and 1993 eruption 353 products (e.g., Matthews et al., 1994, 1999). The bulk-rock composition range for 354 Lascar is wider in the published literature, ranging from andesitic to dacitic 355 $(SiO_2 < 56.6 - 69.4 \text{ wt}\%, K_2O = 1.3 - 3.8 \text{ wt}\%)$ and falling within the fields of CA and 356 HK-CA series (Deruelle, 1982; Matthews et al., 1994, 1999; Mamani et al., 2010) 357 (Fig. 2a). 358

Lascar trace-element rock compositions exhibit smaller light rare earth 359 elements (LREE) enrichments when "N" is normalized to the C1 chondrite values 360 from McDonough (1995) (La/Yb_N=11.2-13.2). The Eu anomaly is small and 361 constant (Eu/Eu*=0.80-0.86). Lascar rocks are slightly enriched in large-ion 362 lithophile elements (e.g., Cs, Rb, and Ba) relative to N-MORB, and they overlap 363 with E-MORB. Most samples have low contents of the high-field-strength 364 elements (HFSE) Ta, Nb, Zr, and Hf. The Lascar rocks exhibit moderate Ba/La_N 365 366 and U/Th_N values, ranging from 35.9-41.4 and 0.24-0.28, respectively (Table 2). 367

368 4.1.2 Lastarria volcano

369 Figure 2b plots the bulk-rock compositions of our Lastarria samples in the context of the results obtained in previously reported studies. Our samples are 370 intermediate to felsic (SiO₂=58.2–63.4 wt%, K₂O=2.0–3.1 wt%) (Table 2), and fall 371 within the same HK-CA series evolutionary trend (Mamani et al., 2010) defined 372 by bulk-rock literature data (SiO₂=58.6–69.4 wt%, K₂O=2.0–3.8 wt%; Naranjo, 373 1992; Stechern et al., 2017) (Fig. 2b). Our LRA3 and LRA2 samples are among 374 the least-differentiated Lastarria rocks (Naranjo, 1992), while sample LRA4 375 (taken from Ignimbrite 1 emitted by crater 3) is more evolved (SiO₂=63.4 wt%). 376 Our sample LRA4, although evolved, has a lower silica content than the most-377 differentiated Lastarria group of samples: the Negriales lava field (Naranjo, 1992; 378 Fig. 2b). Overall, our rock samples (LRA2, LRA3, and LRA4) are alkali-rich 379 (>5.3 wt%) and have low Mg# values (<53.0%). 380

Trace elements in Lastarria rocks show moderate LREE enrichments (La/Yb_N=25.4–30.1), small Eu anomalies (Eu/Eu*=0.73–0.82), and are richer in large-ion lithophile elements (e.g., Cs, Rb, and Ba) compared with Lascar. Most samples have low contents of HFSE, but the concentrations are slightly higher than those at Lascar (Table 2). The Lascar rocks exhibit moderate Ba/La_N and U/Th_N values (27.9–32.0) and low U/Th_N values (0.23–0.24) (Table 2).

387

388 **4.2 Petrography and mineral chemistry**

389 4.2.1 Lascar volcano

390 The phenocryst concentration decreases in the following order at Lascar: 391 plagioclase > Cpx > Opx > olivine > magnetite. Dome fragments (LAS1) are 392 nonvesicular and densely microporphyric. Scoriae fragments (LAS1 and LAS2) with sizes from lapilli to bomb are all porphyric, but they exhibit various degrees 393 of vesicularity. The LAS1 xenocrystals represent a coarse granulate cumulate of 394 Cpx-plagioclase assemblage found in the dome fragment. The major-element 395 concentrations from those cumulates are compared with the rest of the Cpx and 396 plagioclase found as dispersed porphyric mineral phases in Figs. 3 and 4. The 397 full results obtained in the mineral chemistry analyses of Lascar and Lastarria 398 samples are reported in Appendixes II–V and illustrated in Fig. 3. 399

The LAS1 dome fragments mainly contain porphyric plagioclases (An_{46-60}) 400 401 and green Cpx here identified as augite species (Wo₃₈₋₅₀En₃₉₋₄₆Fs₈₋₁₄) with 402 moderate Mg# values (Mg/(Mg+Fe)=71-86%, average 81%; Fig. 3c). Cpx of 1993 materials (LAS1) are closer to the diopside endmember than to augite (e.g., 403 404 Linsley, 1983). Three of seven core-rim Cpx pairs show normal zoning, but the rest have homogeneous compositions, while four of five core-rim pairs for LAS1 405 crystals show normal zoning (Fig. 3c). Three of six samples of LAS2 augite 406 phenocrysts have normal zoning, while five LAS3 core-rim pairs have reverse 407 zoning, five have normal zoning, and one is homogeneous. The greenish Cpx 408 found in LAS3 (augite; $Wo_{41-52}En_{40-46}Fs_{6-15}$) have moderate Mg# values (81±5%) 409 and compositions similar to that of LAS2 (Fig. 3c). Matthews (1994) reported that 410 1993 scoria and pumice exhibit lower Mg# values of 73-78% and 73-82%, 411 412 respectively.

In the dark scoria of the 1993 eruption (LAS1), pyroxenes-plagioclase granular cumulates are found with similar compositions to phenocrysts of augite sampled in the rest of the rock fragments ($Wo_{40-53}En_{39-46}Fs_{5-17}$ with Mg#=71– 87% and 80±5%) and plagioclase (An_{46-70}). One distinction is that the plagioclases in cumulates are rather heterogeneous and richer in Na, with few crystals reaching consistency with the andesine group (Fig. 3f, Appendix IV).

The LAS2 scoria fragments have An_{43-47} plagioclases and abundant green Cpx (augite; $Wo_{39-50}En_{40-45}Fs_{6-16}$) with moderate Mg# values (72–90%, 78±6%). In comparison, the LAS3 older scoria fragments contain labradorites (An_{47-58}).

Opx minerals are less abundant (Fig. 3a), with hypersthenes as the 422 423 dominant species. Sample LAS1 from dome fragments contains hypersthenes $(Wo_{2-4}En_{68-70}Fs_{20-29})$ with moderate Mg# values (71–77%, 75±3%). A particularly 424 interesting finding is that the hypersthene core-rim pairs have Mg# values similar 425 to those of the 1986–1990 Lascar dome samples (69–77%) reported by 426 Matthews (1994). The hypersthenes from LAS2 scoriae show wide Mg# ranges 427 (64-82%). LAS3 scoria hypersthenes have similar compositions (Wo₂₋₃En₆₄₋ 428 $_{83}$ Fs₁₃₋₃₃) with moderate Mg# values (66–86%, 75±6%) and thus are similar to 429 the crystals of 1993 scoriae. The Mg# values increase moderately from the core 430 431 to the rim (Fig. 3a).

The olivines in dome samples were abundant and primitive (Fo_{76–90}, Fo_{83±4%}; Fig. 3e). Olivines were not analyzed in the LAS2 scoria and can only be observed under a microscope. The olivines in older scoria (LAS3) are abundant and slightly less primitive (Fo_{76–86}, Fo_{80±4%}; Fig. 3e). Only 1 of 18 olivines show reverse zoning, while the rest show forsterite contents decreasing from the core to the rim (Fig. 3e). 439 **4.2.2 Lastarria volcano**

Scoriae and pumice blocks have distinct phenocryst assemblages at 440 Lastarria, with a porphyritic texture and a wide range of microphenocryst (void-441 442 free) concentrations in the LRA2, LRA3, and LRA4 samples. The phenocryst concentration decreases in the following order: plagioclase > Cpx > Opx > biotite 443 > hornblende (trace) > magnetite. Very few olivine crystals were observed as 444 phenocrysts. Scoriae fragments with sizes ranging from lapilli to bombs are 445 highly vesicular (small pores), and the groundmass is generally microcrystalline 446 to glassy. Pumices have various colors and show signs of mingling, with frequent 447 interconnections between clear and dark bands (e.g., Naranjo, 1992; Stechern et 448 al., 2017). 449

The mineral assemblage indicates differentiated magmas at Lastarria (forsterite-olivine, Fo₈₂; augite, Wo_{41–48}En_{38–44}Fs_{9–14}; hypersthene, Wo_{1–3}En_{62– $_{70}$ Fs_{23–35}; plagioclase, An_{38–52}). Substantial compositional dissimilarities exist between different LRA1, LRA2, LRA3, and LRA4 samples (Fig. 3d). Amphiboles and apatites are found also as phenocrysts with spinel/magnetite inclusions and intergrowth (see Stechern et al., 2017).}

The LRA2 scoria blocks contain high concentrations of porphyric plagioclases (An_{22-26}), while plagioclases in pumice fragments from LRA4 appear more evolved (An_{37-52}). Few plagioclases were analyzed overall (n=5). Stechern

438

et al. (2017) classified plagioclases as labradorite and andesine, similarly to the
present study (Fig. 3f, Appendix IV).

Scoria LRA2 samples contain Cpx identified as augite species (Wo42-461 46En39-44Fs11-15) with moderate Mg# values (73-81%, 77±2%; Fig. 3d). The 462 augites are slightly more primitive in LRA3 pumices (Wo₄₁₋₄₈En₄₀₋₄₅Fs₉₋₁₅ with 463 Mg#=74–83%) than LRA4 ($Wo_{42-45}En_{42-44}Fs_{12-15}$ with Mg#=74–78%). For core-464 rim pairs in LRA2, three of nine phenocrysts exhibit reverse zoning while the rest 465 are homogeneous. In LRA3, 10 core-rim pairs comprise 3 with reverse zoning, 3 466 467 with normal zoning, and 4 that are homogeneous. In LRA4, three of six phenocrysts exhibit reverse zoning while the rest are homogeneous. 468

In LRA2, Opx were analyzed and identified as hypersthene species (Wo₁₋ $_{3}En_{73-83}Fs_{14-24}$; Mg#=70%). In pumice fragments from LRA3 fragments, hypersthenes are found as intergrowth Cpx-Opx crystals (Wo₃En₈₃Fs₁₄), whereas augites are more differentiated (Wo_{2,3}En₇₃₋₇₄Fs₂₂₋₂₄). In LRA4, pumice fragments contain hypersthenes (Wo_{2,3}En₆₇₋₇₄Fs₂₅₋₃₃) with moderate Mg# values (66–73%). Zoning does not appear frequently (being observed in only 6 of 18 samples, mostly in LRA4), among which 2 of 6 crystals show reverse zoning.

Micas are frequent in pumice fragments and include several large glass inclusions, but many contain plagioclase and pyroxene solid inclusions. The Fe contents estimated from stoichiometric calculations (Deer, 1992) indicate that most micas have Fe/(Fe+Mg) ratios of 0.28–0.32 (Appendix V). Those ratios are thus close to the phlogopite–biotite transition (Fe/(Fe+Mg)=0.33). Micas have Si/Al^(IV) ratios of 2.40–2.48. 482

483 **4.3 Glass inclusions and matrix glass compositions**

484 **4.3.1 Lascar volcano**

Matrix glasses around phenocrysts were probed to verify mineral-liquid 485 equilibrium (Appendix VI). Spherical and ellipsoidal glass inclusions were also 486 observed and analyzed, but the differentiated nature of those inclusions 487 (SiO₂=73.8–76.8 wt%, K₂O=3.5–4.2 wt%; Fig. 2a) made it difficult to use them for 488 barometry calculations (see below). Only hypersthene and augite euhedral 489 490 crystals have fully enclosed glassy inclusions without postentrapment characteristics, so their major-element compositions are likely to be unaffected by 491 elemental diffusion in crystal hosts (Danyushevsky et al., 2004). The crystal host 492 compositions are listed in Appendix VII. 493

Lascar matrix glasses are andesitic to trachytic and follow steep K-versus-494 Si evolution trends (Fig. 2a; SiO₂=61.0–72.1 wt%, $K_2O=1.0-5.1$ wt%). The most-495 primitive glasses are found around hypersthene minerals from dome fragments 496 (SiO₂=61.0-70.0 wt%, K₂O=1.0-4.5 wt%, Mg#≤36%), while most Cpx and 497 plagioclase glass rims are trachytic to rhyolitic. Figure 4a demonstrates that 498 magnesium distribution coefficients measured from sets of mineral-glass couples 499 500 are below olivine (Kd_{Fe-Ma}=0.30±0.03) or Cpx (Kd_{Fe-Ma}=0.27±0.03) equilibrium values, with a few exceptions. The Cpx-plagioclase cumulates contrast the most 501 from the mineral-liquid Kd being in equilibrium (Fig. 4a), and so they were 502 considered as xenocrystals in this study. 503

504

505 4.3.2 Lastarria volcano

Lastarria matrix glasses exhibit andesitic, banakitic, and trachytic compositions (SiO₂=62.3–76.6 wt%) and are particularly rich in K (K₂O=2.3–5.6 wt%). Hypersthene glass rims exceptionally show evolved rhyolitic compositions (SiO₂>75.5 wt%, K₂O>5.0 wt%, Mg#<26.3%), and are richer in alkalis compared with Lascar (Fig. 2b, Appendix VI).

511 Spherical and ellipsoidal glass inclusions are also rather evolved 512 $(SiO_2=53.7-75.9 \text{ wt\%}, K_2O=0.6-6.0 \text{ wt\%})$. Opx, Cpx, and biotite crystals have 513 fully enclosed glass inclusions without postentrapment characteristics. The 514 crystal host compositions are listed in Appendix VII, and the mineral host 515 compositions from biotite are listed in Appendix V.

Distribution coefficients for Fe are closer to equilibrium values than for the Lascar samples (Fig. 4). In total, two inclusions and three glasses cross the equilibrium lines within the margin of error. Equilibrium is reached for those samples with maximum Fe^{3+}/Fe^{2+} ratios (1.16±0.16) and minimum Mg# values.

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521 **4.4 Element and isotope compositions of noble gases**

522 **4.4.1 Fumaroles**

Two dry gases were collected from a single high-temperature fumarole on the lower field at the base of Lastarria cone (5,030 m a.s.l.). The two samples yielded reproducible results (for He and Ne; Ar was analyzed in only one sample), which are presented in Table 3. In detail, the He concentrations were 9.6 and 10.8 ppm, while the Ne concentration was 0.06 ppm in both samples (the corresponding

⁴He/²⁰Ne ratios are 157 and 176). These results are comparable to those 528 reported by Lopez et al. (2018) for samples obtained during the same sampling 529 campaign. The ⁴⁰Ar concentration was 75 ppm, with an ⁴⁰Ar/³⁶Ar ratio of 315 530 (Table 3). He/Ne and Ar isotope data indicate the presence of moderate-to-531 severe air contamination, since the ⁴⁰Ar/³⁶Ar ratio remains slightly above the 532 theoretical ratio in atmosphere (⁴⁰Ar/³⁶Ar=295.5; Ozima and Podosek, 2002). ⁴⁰Ar 533 was thus corrected for air contamination (⁴⁰Ar*) assuming that the ³⁶Ar present in 534 our samples was derived from atmosphere, as follows: 535

536
$${}^{40}\text{Ar}^* = {}^{40}\text{Ar}_{\text{sample}} - ({}^{36}\text{Ar}_{\text{sample}} \times ({}^{40}\text{Ar}/{}^{36}\text{Ar})_{\text{air}})$$

537 The ³He/⁴He values corrected for atmospheric contamination (Rc/Ra) are 5.3 and 538 5.4 Ra (Figs. 5 and 6).

539 Fumaroles at Lascar volcano were not sampled in this study, and so below 540 we only consider literature data for comparison with our measures in FIs.

541

542 4.4.2 Fluid inclusions

The concentrations and isotope ratios of noble gases in FIs are reported in 543 Table 4. The LAS3 rock samples were the only ones from Lascar volcano where 544 it was possible to hand pick sufficient olivines for measuring noble gases. The 545 resulting noble-gas concentrations were 2.5×10^{-13} mol/g for He (Fig. 5), 1.1×10^{-14} 546 mol/g for Ne, and 7.4×10^{-12} mol/g for Ar (Table 4). Cpx from the same sample 547 showed a comparable amount of He $(3.2 \times 10^{-13} \text{ mol/g}; \text{Fig. 5})$ but higher Ne and 548 Ar contents $(5.8 \times 10^{-14} \text{ and } 9.2 \times 10^{-12} \text{ mol/g, respectively})$, thus indicating greater 549 air contamination. Fls from LAS1 Cpx xenocrystals from cumulates (see 550

551 Section 4.3.1) displayed He, Ne, and Ar ranges of concentrations of $2.0-2.9 \times 10^{-13}$, $1.2-22.7 \times 10^{-14}$, and $1.1-3.6 \times 10^{-12}$ mol/g, respectively (Fig. 5).

553 Among Lastarria samples, only in LRA3 it was possible to hand pick 554 sufficient olivines for measuring noble gases; the other samples were analyzed 555 for Cpx only. The He, Ne, and Ar concentrations in olivine FIs were 3.1×10^{-13} , 556 5.6×10^{-15} , and 3.7×10^{-12} mol/g, respectively (Fig. 5, Table 4). FIs from Cpx in 557 LRA2, LRA3, and LRA4 yielded He, Ne, and Ar concentrations of $0.2-6.6 \times 10^{-13}$, 558 $2.1-2.5 \times 10^{-14}$, and $2.4-4.8 \times 10^{-12}$ mol/g, respectively (Fig. 5, Table 4).

The ${}^{4}\text{He}/{}^{20}\text{Ne}$ and ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ ratios had ranges of 5.6–21.7 (Fig. 6) and 559 300-310, respectively, in Lascar samples, and of 1.0-55.4 (Fig. 6) and 302-308 560 in Lastarria samples. The ³He/⁴He ratios corrected for atmospheric contamination 561 (Rc/Ra) vary between 6.9 and 7.3 Ra in olivines and Cpx from LAS1 and LAS3, 562 while they are lower (5.2-5.4 Ra) in LAS1 Cpx xenocrysts (Fig. 5). Among 563 Lastarria samples, the ³He/⁴He ratios vary between 5.3 and 8.0 Ra (Fig. 5). The 564 ratio was highest for LRA3 olivines and lowest for LRA4 Cpx (Table 4). It should 565 be noted that a strong atmospheric correction was found for LRA2 Cpx, with a 566 marked difference between R/Ra and Rc/Ra (⁴He/²⁰Ne=1.0). This sample has the 567 lowest He content $(2.4 \times 10^{-14} \text{ mol/g})$ and the lowest ⁴He/⁴⁰Ar^{*} (see Section 5.2.2), 568 which could indicate diffusive fractionation of He from the crystal (e.g., Nuccio et 569 al., 2008; Rizzo et al., 2018). Due to this possible secondary effect, we ignore 570 this sample in the discussion below (see Table 4). 571

572

573 5. Discussion

574 **5.1 Geothermobarometry of the plumbing system**

575 We initially used pairs of mineral–liquid compositions to estimate the 576 pressure/temperature (P/T) conditions of crystallizing magmas under the Lascar 577 and Lastarria volcanoes. To achieve this aim we utilized major oxide 578 concentrations as input parameters in different mineral–liquid equilibrium 579 geothermobarometers (see Appendixes VI and VII, and below).

580

581 5.1.1 Lascar volcano

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According to the estimated P/T conditions for magmas at Lascar, we 583 propose a derived equivalent lithostatic pressure model with a minimum of three 584 separate intrusive events occurring since ~9.5 ky. Each intrusion represents an 585 ascending melt inside a crystal mush system (i.e. Marsh, 1995), keeping a 586 magma chamber morphology is not conditional, but evolving vertically in the 587 lithospheric crust. We assume those magmas have been following an isothermal 588 decompression phase and a decompression/extended cooling phase, as 589 observed in the P/T diagram (Fig. 7a). These two-step intrusive phases represent 590 all sampled products (LAS1, LAS2, and LAS3) that crystallized magma with a 591 two-pyroxene equilibrium for different storage zones and covering a depth of at 592 593 least 41 km in the lithosphere (Fig. 7a).

594 Three mineral–liquid thermobarometer data sets were obtained for Cpx-595 Opx, clinopyroxene–liquid (Cpx-L), and orthopyroxene–liquid (Opx-L) pairs. In 596 detail, the Cpx-Opx thermobarometer and mineral chemistry data indicate hypersthene and augite species at Lascar with compositions that are consistent
with thermodynamic equilibrium at 642–649 MPa and 1079–1092 °C (Fig. 7a,
Appendixes VI and VIII). The Cpx-L temperatures for Lascar are correlated with
the pressure changes expressed by Equation 32d in Putirka (2008), ranging from
1067 to 1181 °C (1108±32 °C, n=8), while the range of Opx-L temperatures
(Equation 28a in Putirka, 2008) is 875–1023 °C (913±70 °C, n=5).

The Cpx-L pair are in equilibrium for LAS1 output pressures between 305 603 and 546 MPa, except for LAS1 augite cumulates (xenoliths) that are chemically 604 605 far from the Kd equilibrium and farther than the other mineral-liquid Mg# pairs (Fig. 4a). LAS1 hypersthene pressures reach 542 MPa, while the LAS2 scoriae 606 reach 390 MPa (Fig. 7a). This is likely to correspond to maximum pressure 607 conditions since none of these crystals have their rim composition in equilibrium 608 with the surrounding glass. In LAS3, we infer pressures between 85 and 660 609 MPa for augite equilibrium, and its association with hypersthenes (as trapped 610 solid inclusions) indicate that intergrowth of the two phases is possible under 611 equilibrium conditions (Fig. 7a). For hypersthene and augite, we find an overall 612 better Mg# equilibrium between the glass rim versus phenocryst rim 613 compositions (Fig. 4a). Consequently, the crystallization sequence implies 614 equilibrium of mafic minerals (Cpx or Opx) with the surrounding melts at depth 615 616 between 4 and 22 km (Fig. 7). To illustrate the magmatic evolution that produced Cpx-Opx crystals, we thus propose the existence of an area with deep mafic 617 magma reservoirs that would represent the ranges of lithostatic pressure depths 618 619 shown in Fig. 10a. Lower pressure values (<305 MPa) would represent the plagioclase appearance controlled during the decompression cooling phase of
the same ascending magma body (see Fig. 4a). This is likely to occur at
shallower levels, possibly corresponding to the pounding zone illustrated in
Fig. 10a.

Some peculiarities persist in the most-recent intrusive sequences. 624 Regarding the mineral chemistry and glass compositions at Lascar, the 1986-625 1990 collapse of dome growth (LAS2) could represent distinct intrusive events, 626 with magma being slightly more differentiated than for the 1993 explosive 627 628 sequence (LAS1) (Fig. 10a). Crystals of dome growth also show Mg# heterogeneities, as evidenced by bimodal mafic mineral values (Mg# for olivine, 629 hypersthenes, and augite; Fig. 3a). The 1989-1990 dome fragments represent a 630 magmatic intrusive phase presumably with low cooling rates and longer 631 residence time in the superficial 2-km-deep ponding zone below the central crater 632 (Stechern et al., 2017). In contrast, the emitted scoria (LAS1) present in the 633 pyroclastic flow of the 1993 eruption represents a direct and fast magmatic 634 ascent. 635

Uncertainty also remains about the origin of trachitic-to-rhyolitic glass compositions probed on the mineral–glass pairs of our Lascar samples (Fig. 2a). This implies the possibility of encountering distinct intrusive events or residual differentiated melts that derive from a previous intrusive event (Fig. 10a). Such differentiated products have already been reported for emissions from the central crater and eastern vents of Lascar (Matthews et al., 1999; Gardeweg et al., 2011). For example, the range of glass compositions found in our study (Fig. 2) is 643 close to the 1993 andesite scoria-dacitic pumice reported by Matthews et al. (1999), with SiO₂=62–65 wt%. In addition, white pumices with felsic compositions 644 were found in the lithic-rich and pumice-rich lenses of the 1993 pyroclastic 645 deposits (Sparks et al., 1997; Calder et al., 2000). Those evolved magmas 646 probably reflect the trachitic-to-rhyolitic matrix glass compositions observed in the 647 present study (e.g., SiO₂=72–73 wt%; Fig. 2a). We cannot exclude the possibility 648 that those glasses result from extended differentiation from previous and esitic-to-649 dacitic magmas that intruded into the eastern Lascar edifice from 7.1 ky up to the 650 651 present day.

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653 **5.1.2 Lastarria volcano**

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mineral-liquid thermobarometer data sets show The three 655 that cooling/decompression behaviors affect Lastarria as they do Lascar (Fig. 7, 656 Appendix VIII). Based on those results and the evolution of P/T parameters, we 657 derived an equivalent lithostatic pressure model for the magmas that produced 658 Ignimbrites 1 and 2 since ~4.85 ky A.P. (Fig. 10a). The most-recent Ignimbrite 3 659 (which is younger than ~2.46 ky) did not have mineral-liquid Kd_{Fe-Ma} in 660 equilibrium in our samples, and so its thermodynamic condition parameters were 661 662 based on the data of Stechern (2017). No equilibrium pressures were encountered for LRA1 and LRA2, which were associated with Group C in 663 Stechern et al. (2017) that corresponds to a source at a depth of ~20-40 km. 664

665 The detailed P/T data show hydrous Cpx-L pressures that are particularly variable at Lastarria, ranging from 989 MPa down to 199 MPa, with Kd_{Fe-Ma} being 666 in equilibrium (Fig. 7b, Appendix VIII). Hypersthenes are in equilibrium from 667 390 MPa down to <42 MPa at Lastarria (hydrous melts; Putirka, 2005, 2008; 668 Lange et al., 2009). At Lastarria the Cpx-L temperatures are 1135-1147 °C 669 (1140±38 °C, n=6), while those of Opx-L are 904–935 °C (921±13 °C, n=6). 670 Many results for the tested Cpx-L and Plagioclase (Pgl)-L thermobarometric pairs 671 follow vertical pressure decreases for relatively constant temperatures 672 673 (isothermal decompression; Fig. 7, Appendix X).

Hypersthene, augite, and plagioclase species were found on thin sections 674 and in the mineral chemistry analyses under various P/T conditions (Fig. 7b). 675 Amphibole and biotite minerals were also identified, which support the presence 676 of late crystallization conditions at superficial crustal levels at Lastarria (e.g., no 677 amphibole present at depths >20 km according to Stechern et al., 2017). This 678 indicates that magma evolution occurs at various depth ranges beneath 679 Lastarria. The complex data related to the crystallizing magma reservoir beneath 680 681 this volcano indicate that static magmas evolve both under deep and superficial conditions. 682

Overall, the data produced by this study support the frequent occurrence of mixing of variably differentiated materials in Lastarria magmas at different depth zones (up to 32 km) from >4.8 to 2.5 ky Ignimbrite sequences (Ignimbrites 1 and 2; Naranjo, 2010). Depth zones for mixing (e.g., Naranjo, 1992) with mafic endmembers were identified between 6.5 and 18 km by
Stechern et al. (2017), and they are supported by our data obtained from the mineral chemistry analyses and our observed mingling bands of clear and dark tones from LRA3 and LRA4 pumices. The scenario of mafic magma injection and mixing of different endmember compositions is supported by our scoria and pumice fragments of different ages (<4.8 ky), where inverse zoning is present in mafic minerals (Fig. 3b, d, f). This is evidenced in various single core–rim pairs of Mg# values of single phenocrysts (Appendixes II–V).

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- 696

697 5.2 Primitive magma with stronger MORB signature modification at
 698 Lastarria volcano

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The findings from the bulk-rock analyses of our samples were compared at 700 Lascar and Lastarria volcanoes to verify the magma affinity and characterize the 701 extent of differentiation from primitive magmas (Tables 1 and 2). Lascar volcano 702 magmas show an Andean-continental-island-arc affinity for HFSE and transition-703 704 metal ratio (Sc/Ni) markers, while trace elements from Lastarria are typical of Andean magmatism in our samples (Fig. 8). The mafic origin of most Lascar 705 products reflect a different type of magma differentiation, such as being less rich 706 707 in K and corresponding to an homogeneous source, and so restricted to a typical volcanic arc signature (Fig. 8). The tectonic environment signature is similar, but 708 even though the data set is very small, the La/Yb ratios clearly demonstrate that 709 710 the cortical contribution is greater for Lastarria where elevation and crust thickness are expected to be greater (Thorpe et al., 1982; Hildreth and Moorbath,
1988; Stern, 2004). This highlights the common association with Andean K-rich
magmas (Stern, 2004).

To verify if the MORB signature of magma was modified, bulk-rock results were plotted in a discrimination diagram where lines divide subduction from nonsubduction settings and arrows point to MORB and within-plate granite endmembers (Fig. 8b). The purple star in the figure indicating primordial mantle is from Bowden et al. (1984), which approximately divides ocean arcs from active continental margins. The evolution of K_2O/Yb versus Ta/Yb shows that both volcanoes emit products affected by fractional crystallization (Fig. 8b).

The concentrations of trace elements and REEs from bulk-rock analyses of 721 both Lascar and Lastarria share familiar characteristics, such as both 722 representing typical MORB and tholeiitic series. Since bimodal mantle and crustal 723 magma origin are identified at Lastarria and are typical of Andean rocks, we 724 suggest that various local factors can affect the bulk-rock chemistry and be 725 superimposed over MORB signatures (Davidson and de Silva, 1992). The plate-726 727 rock enrichment in an intercontinental context probably reflects a certain mantle MORB signature modification at Lastarria via crustal contamination during 728 episodes of magma stagnation (Fig. 8b). The composition variations are 729 730 concordant with longer magmatic cycle pauses between Ignimbrites 1, 2, and 3, to at least three extrusive events occurring since ~4.9 ky (Naranjo, 2010). This 731 chemical variation is far from reflecting large-volume Andean ignimbrites emitted 732 733 during long-term tectonic cycles covering millions of years (e.g., de Silva et al.,

2006; Scott et al., 2018; Wörner et al., 2018), and so bulk-rock chemistry
contamination at the scale of the vertical plumbing system may represent
basement heterogeneities (Wörner et al., 1994; Haschke et al., 2006).

At Lascar this dual chemical characteristic is not present in the magmas that 737 has intruded into the crust since ~9.5 ky, at least for the samples analyzed in the 738 present study, since Fig. 8 shows a typical volcanic arc signature with a lower 739 cortical influence (low K₂O/Yb and La/Yb ratios). The chemistry of bulk rock 740 represents a less-contaminated composition of one particular major magmatic 741 cycle during the 1980s and 1990s and an older volcanic event from the 742 Holocene. This extent of MORB modification from Lascar magma probably 743 represents shorter residence times for the "crystal mush" systems modeled in 744 Fig. 10. 745

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748 **5.3 Geochemistry of fumarole gases and Fls**

749 5.3.1 Atmospheric contamination

The ⁴He/²⁰Ne and ⁴⁰Ar/³⁶Ar ratios of fumarole gases and FIs highlight a variable extent of air contamination. Fumarole gases from Lastarria and Lascar display the minor addition of air relative to FIs, as indicated by their higher ⁴He/²⁰Ne (Fig. 6) and ⁴⁰Ar/³⁶Ar (Tables 3 and 4) ratios. This suggests that FIs were entrapped by recycled fluids in contact with the atmosphere, such as mixing with water that circulates in the form of conductive hydrothermal cells in contact with intrusive magmas (Fig. 10). It is more likely that FIs entrapped air under posteruptive conditions (during magma cooling) via mineral fractures (Nuccio etal., 2008).

The ⁴He/²⁰Ne and ⁴⁰Ar/³⁶Ar ratios measured in fumarole gases from 759 Lascar and Lastarria volcanoes are far from typical MORB-like values 760 (⁴He/²⁰Ne>1000 and ⁴⁰Ar/³⁶Ar≤44,000; e.g., Burnard et al., 1997; Ozima and 761 Podosek, 2002). This indicates that an atmospheric component is involved in the 762 763 local magmatic and/or mantle source. These ratios actually fall within the range 764 of values measured in other arc volcanoes worldwide (Hilton et al., 2002; Shaw 765 et al., 2003, 2006; Martelli et al., 2014; Di Piazza et al., 2015; Rizzo et al., 2015; Robidoux et al., 2017; Battaglia et al., 2018). This evidence reinforces the idea 766 767 that atmospheric components are also recycled into the mantle by subducting slabs. 768

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5.3.2 Inferences on the mantle sources beneath Lascar and Lastarria volcances

We evaluated the geochemical features of magmatic/mantle sources beneath Lascar and Lastarria by focusing on ${}^{3}\text{He}/{}^{4}\text{He}$ corrected for air contamination (Rc/Ra). We also considered ${}^{4}\text{He}/{}^{40}\text{Ar}^{*}$, when available, because this parameter can track magmatic degassing in phenocrysts and fumaroles. This is because He is around 10 times more soluble than Ar in silicate melts, although this difference can vary due to the chemistry and pressure of magmas, leading eventually to ${}^{4}\text{He}/{}^{40}\text{Ar}^{*}$ increasing especially during the late stages of degassing (e.g., laconoMarziano et al., 2010; Boudoire et al., 2018). It should be noted that the ${}^{4}\text{He}/{}^{40}\text{Ar}^{*}$ ratio in the upper mantle is typically within the range of 1–5 (Marty, 2012).

As reported in Sections 4.4.1 and 4.4.2, the cogenetic olivine and Cpx 781 782 from LAS1 and LAS3 show Rc/Ra values between 6.9 and 7.3 Ra, while Cpx xenocrysts of LAS1 display lower values of 5.2-5.4 Ra(Figs. 5 and 6). The 783 ³He/⁴He ratios measured in LAS1 and LAS3 phenocrysts are comparable to the 784 range of values measured in fumarole gases by Tassi et al. (2009) (6.5-7.3 Ra), 785 suggesting that fumarole gases from Lascar are representative of the local 786 magmatic source (see Fig. 10a) and do not experience any shallow 787 contamination (e.g., in the hydrothermal system) by crustal-derived ⁴He. Instead, 788 the lower value measured in Cpx xenocrysts from LAS1 probably reflects 789 contamination by crustal-derived ⁴He, which is accentuated by the low ³He/⁴He 790 values of xenocrysts from LAS1; this result for a magma that differentiated and 791 degassed over a long time period favors the production and accumulation of 792 radiogenic ⁴He from basement rocks. This hypothesis is reasonable since LAS1 793 xenocrysts represent augite cumulates that may have experienced a lower 794 cooling rate and a longer residence time for the dome fragment formed during 795 1989-1990. This idea is qualitatively supported by the ⁴He/⁴⁰Ar* ratio, which is 796 lower (${}^{4}\text{He}/{}^{40}\text{Ar}^{*}$ =1.2–2.1) in samples displaying the highest ${}^{3}\text{He}/{}^{4}\text{He}$ ratios (LAS1 797 and LAS3) than in xenocrysts from dome fragment LAS1 (⁴He/⁴⁰Ar*=5.0–6.0). 798

In the case of Lastarria volcano, FIs showed ${}^{3}\text{He}/{}^{4}\text{He}$ ratios between 5.3 and 8.0 Ra (Figs. 5 and 9). The highest value (8.0 Ra) was uniquely measured in the olivine of LRA3, while lower values (5.3–6.6 Ra) were measured in Cpx of

LRA3 and LRA4, which represent Ignimbrites 1 and 2 (Table 4). The fumarole 802 gases analyzed in this work have a mean ${}^{3}\text{He}/{}^{4}\text{He}$ ratio of ~5.3 Ra, which is 803 within the range of previous fumarole measurements (4.6-6.2 Ra) by Aguilera et 804 al. (2012) and Lopez et al. (2018) (Figs. 5 and 10b). We argue that FIs of olivine 805 reflect a more-primitive signature of ³He/⁴He than Cpx and fumarole gases. 806 These latter samples seem to reflect a later (shallower) stage of magma 807 degassing before the series of ignimbrites is produced (Fig. 10b), with sizeable 808 crustal contamination by crustal-derived ⁴He in the shallower parts of the volcano 809 plumbing system. The evidence from petrography and mineral chemistry 810 indicates multistep ponding of magmas that could explain the observed variability 811 in ${}^{3}\text{He}/{}^{4}\text{He}$ ratios between olivine and Cpx. 812

In order to draw conclusions about the local mantle source, we consider 813 the highest ³He/⁴He values measured in FIs from Lascar and Lastarria. The 814 ³He/⁴He value of 7.3 Ra measured in FIs from Lascar falls within the lower end of 815 the MORB range (8±1 Ra; Graham, 2002), while that of 8.0 Ra in FIs from 816 Lastarria is around the middle of the MORB range (Figs. 5 and 6). These values 817 fall within the range of typical ratios reported for some volcanic arc segments 818 worldwide independently of sediment contributions or the presence of a 819 serpentinized oceanic plate (e.g., central and northern Chile, Peru, and Ecuador, 820 Kamchatka, and the Kuriles Island; Hilton et al., 2002; Völker et al., 2013; 821 Jacques et al., 2014). Nevertheless, recent studies of ³He/⁴He in FIs from rocks 822 erupted in the Central American Volcanic Arc (CAVA) suggest that slight but 823 824 appreciable differences (of 0.5–1.0 Ra) could reflect contamination of the source by subducting sediments bearing U and Th (Di Piazza et al., 2015; Robidoux et al., 2017; Battaglia et al., 2018). This means that the mantle beneath Lastarria is either not contaminated or is less contaminated than that beneath Lascar, as observed in other arc volcanoes of the CAVA (Turrialba and Pacaya; Di Piazza et al., 2015; Battaglia et al., 2018). An alternative explanation is that the magmatic dynamics are more active beneath Lastarria than Lascar, and the ³He/⁴He difference between the volcanoes is attributable to crustal contamination.

More generally, the ³He/⁴He ratios measured in FIs from Lascar and 832 Lastarria are higher than the maximum values reported for central and northern 833 Chile (6.84 and 6.02 Ra, respectively; Hilton et al., 1993) and comparable to the 834 highest values measured in the Planchón-Peteroa volcano (7.1 Ra; Tassi et al., 835 2016) and the Copahue-Caviahue volcano (7.9 Ra; Agusto et al., 2013) located 836 in southern Chile. Another consideration that arises from this and past studies of 837 ³He/⁴He in South America is that only fumarole gases from very active volcanoes 838 (i.e., strongly degassing SO₂ into the atmosphere) and FIs in olivine and 839 pyroxene yield values that can be used for extrapolations to mantle features. 840 Instead, ³He/⁴He ratios measured in geothermal fluids and fumaroles from 841 volcanoes exhibiting little activity (with no active SO₂-rich plume) or quiescent 842 volcanoes (e.g., Hilton et al., 1993; Ray et al., 2009; Benavente et al., 2016; 843 844 Tassi et al., 2016 and references therein) are always below the MORB range, indicating variable extents of crustal contamination (Fig. 9). These extents of 845 contamination seem also to be related to how far the gas emissions are from the 846 847 arc front. For example, the fumaroles (n=3) sampled farthest from the active volcanic front fall below the (uncorrected) Ra range of 0.82–6.02 (2.39±1.43)
reported for northern Chile by Hilton (2002). Contrary to central Chile where Ra
progressively increases from north to south with a decreasing contribution from
continental crustal ⁴He (Benavente et al., 2016), there is no clear north–south
variation or a correlation between the values in Peru and northern Chile (Fig. 9).
This Ra variation instead decreases as the thickness of the rigid continental crust
increases toward the east of the Andean cordillera (Gardeweg et al., 2011).

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6. Conclusions

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According to the petrological data from bulk rocks and mineral separates (olivine, 859 ortho-Cpx, and plagioclase) from andesite scorias, the post-1989 Lascar 860 reservoir is fed by a single intrusive event of mafic magmas that bypassed 861 various differentiated magma supplies (potentially magma ponding zones with 862 rhyolitic compositions represented by the pumice rocks; Matthews, 1994; 863 Matthews et al., 1999). A similar scenario may produce the andesitic Tumbres 864 flow, but at the beginning of the Holocene (Gardeweg et al., 2011). Intrusive 865 magmatic bodies are drained in ponding zones at distinct crustal depths identified 866 867 with P/T models as crystallizing Opx equilibrium ranges (390-649 MPa, corresponding to lithostatic equivalent depths [LEDs] of 15–21 km). The magmas 868 ascend rapidly through the crust until reaching a shallow ponding zone where 869 870 Cpx and plagioclases are in equilibrium (from <305 to 741 MPa, corresponding to 871 LEDs ranging from 12–29 km up to 3.4–6.7 km). In contrast, Lastarria is fed by multiple intrusive events (Ignimbrites 1, 2, and 3) that originally took shape under 872 the deepest crustal conditions illustrated by our data set (~500-990 MPa, 873 corresponding to LEDs of ~20-40 km) that encompass the petrological range of 874 values estimated by Stechern et al. (2017). We have identified the minimum 875 depth crustal zones for residual crystallizing magma to equilibrate mafic minerals 876 as 6.5-8 km, which is consistent with Stechern et al. (2017). A superficial mixing 877 zone from 1 to 5-6 km appears to receive the most-differentiated magmas and 878 residual fluids that could explain deformation detected by interferometric 879 synthetic-aperture radar as well as tomographic seismology anomalies (Remy et 880 al., 2014; Diaz et al., 2015; Spica et al., 2015). Overall, the various magma 881 storage levels at Lastarria represent magmatic cycles affected by mixing effects, 882 with inverse zoning from phenocrysts exerting different affects in each distinct 883 magmatic event). 884

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We now combine the information on plumbing system depths with isotope data of 886 887 noble gases measured in fumaroles and FIs from mafic minerals that represent residual magmatic fluids. The two studied stratovolcanoes have distinct parental 888 magma compositions despite the similarities in their explosive volcanic behaviors 889 and geological backgrounds. The Lascar magmatic fluids and parental magma 890 showed some degree of air contamination, with ⁴⁰Ar/³⁶Ar=300-310 and 891 ⁴He/²⁰Ne=5.6–204. The ³He/⁴He ratios (6.91–7.12 Ra) from minerals in scoria 892 893 from any ages (the Tumbres flow in 1993) are homogeneous and slightly lower than those for a MORB-like magmatic source (8±1 Ra; Graham, 2002), suggesting that one type of parental magma is ascending below Lascar independently of the emission sites and crystallization mechanisms. Magmas with longer residence times would necessarily experience lower cooling rates of the crystallizing plug and allow more time for the absorption of more radiogenic ⁴He, such as via crustal contamination after mixing with pristine MORB-like fluids.

The Lastarria magmatic fluids and parental magma also show some degree of air 901 contamination, with ⁴⁰Ar/³⁶Ar=302-308 and ⁴He/²⁰Ne=1.0-55.4. Olivine FIs 902 trapped the most-primitive fluids (8.01 Ra), highlighting the sequence of fractional 903 crystallization between Cpx and olivine phenocrysts (Shaw et al., 2003, 2006). 904 The ³He/⁴He ratios show significant variability of 5.31–8.01 Ra. In this situation 905 we cannot exclude that fluids trapped in olivine reflect different plumbing systems 906 conditions, which could support the hypothesis of crustal contamination by the 907 addition of radiogenic ⁴He; this is probably a common feature below the Lascar 908 and Lastarria edifices considering the large crustal thickness below the CVZ 909 (Trumbull et al., 1999). Bulk-rock traces and REE signatures provide evidence of 910 differentiation and one short magmatic cycle that crystallizes a single type of 911 mantle MORB magma, but the signature is strictly related to volcanic arc features 912 at Lascar (e.g., La/Yb and U/Th values). A high degree of compositional 913 heterogeneity was observed in the bulk-rock data for Lastarria, with variable 914 noble-gas signatures between the distinct magmatic events. 915

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Supplementary data (Appendixes I–X) related to this article can be found online.918

919 Acknowledgments

920 We thank the INGV laboratory staff for providing access and analytical support. We also thank the DiSTeM laboratory at the University of Palermo for supporting 921 this work with internship opportunities at INGV. Special thanks are due to 922 Mariano Tantillo and Mariagrazia Misseri for helping in sample preparation and 923 924 noble-gas analyses, as well as to Piergiorgio Scarlato for allowing access to the 925 HPHT laboratory of INGV in Rome for electron microprobe analysis. We also 926 would like to mention the field participation of Universidad Católica del Norte in 927 Antofagasta and the organizer of the 2014 IAVCEI CCVG 12th Volcanic Gas 928 Workshop in Chile, who made access possible for field rock sampling; that workshop also provided a student travel scholarship of US\$ 1,000. This work was 929 partially supported by the Deep Carbon Observatory. 930

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937 Table and figure captions

938 **Table 1 – Locations.**

939 Listing of sample coordinates along with field and sample petrographic 940 descriptions.

941 **Table 2 – Bulk-rock analyses.**

Bulk-rock major-element compositions were analyzed for major elements, trace elements, and REE using a combined ICP/MS device (WRA4B2) at Ancaster (Code 4B2-Std, Actlabs). Results of bulk-rock analyses of powder samples prepared at the DiSTeM laboratory at the University of Palermo. The measurement detection limits are also listed.

947

948Table 3 – Chemical and isotope compositions of noble gases from949fumaroles.

*UTM Zone 19 (S) at an altitude of 5030 m a.s.l.

Table 4 – Chemical and isotope compositions of noble gases from FIs.

⁹⁵² *Sample with an xenocrystal origin.

953

Figure 1 – Locations. Topographic map and locations of the analyzed volcanoes. (a) Converging Nazca and South America plates (Nazca/SAm) with its subduction vector illustrated using a black arrow representing the NUVEL 1-A model from DeMets et al. (1994). (b) Continental-scale map showing the North Volcanic Zone (NVZ), CVZ, and South Volcanic Zone (SVZ).

959

Figure 2 – Rock classification according to Peccerillo and Taylor (1977). Diagram of K_2O versus SiO₂ for bulk-rock compositions in this study and mineral glass rims and bulk-rock compositions in the literature. Compositional data are for (a) Lascar and (b) Lastarria.

964

Figure 3 – Frequency diagrams of Mg#. Core and rim Mg# values provided for
each crystal in the studied rock samples from Lascar (LAS1, LAS2, and LAS3)
and Lastarria (LRA2, LRA3, and LRA4). (a) Hypersthene from Lascar, (b)
hypersthene from Lastarria, (c) augite from Lascar, (d) augite from Lastarria, (e)

olivine from Lascar and Lastarria, and (f) plagioclase An# contents from Lascarand Lastarria.

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Figure 4 – Crystal versus liquid compositions. Mg# values for liquid (glass) are compared to Mg# values for minerals (hypersthenes and augite are indicated by colored squares and lozenges, respectively). Equilibrium mineral–glass (total Fe) values are plotted along with data from the literature. The results indicate Fe²⁺ (fully black symbols: hypersthenes and augites are indicated by squares and lozenges, respectively). Data are for (a) Lascar and (b) Lastarria.

978

979

Figure 5 – ³He/⁴He ratios corrected for atmospheric contamination (Rc/Ra)
 versus He concentration in Fls. Typical ratios from MORB are 8±1 Ra
 (Graham, 2002). Ranges of published ³He/⁴He values for fumaroles are from
 Tassi et al. (2009) for Lascar and Aguilera et al. (2012) for Lastarria.

984

Figure 6 – ³He/⁴He versus ⁴He/²⁰Ne in fumaroles and Fls. Symbols are as
 indicated in Fig. 5.

Figure 7 – Geobarometers. Graphs of estimated P/T relationship for magma 987 crystallization conditions. The geobarometers include Opx-L and Cpx-L pairs 988 989 from Putirka et al. (2003) and Equation 32c in Putirka (2005) are plotted for Lascar and Lastarria data sets. The Cpx-Opx thermobarometer data are 990 compared when mineral pairs are observed in rock samples (Equations 38 and 991 39 in Putirka et al., 2008). Data sets for plagioclase-liquid pairs (Lange et al., 992 2009) are illustrated with water contents of the liquid melt system listed in 993 994 Appendix VI and VII. The water contents are only known at Lastarria from hygrometer estimates ($H_2O=1-2.1$ wt%) and the solubility model of Newman and 995 996 Lowenstern (2001). Cpx and Opx versus liquid equilibrium geobarometers are 997 estimated in dry and wet conditions (Putirka, 2003, 2005, 2008). Amphibole pressures and temperatures from Stechern et al. (2017) were obtained using 998 999 Ridolfi et al. (2010) for amphibole (1) data, and Ridolfi and Renzulli (2012) for 1000 amphibole (2) models. Data are for (a) Lascar and (b) Lastarria.

1001

1002 Figure 8 – Rock classification diagram. Results from Lascar and Lastarria bulk-rock chemistry analyses. (a) Tectonic discrimination of the andesites (Bailey, 1003 1981). The tectonic discrimination diagrams of La/Yb versus Sc/Ni are from 1004 Bailey (1981), which provide evidence for each tectonic environment while 1005 1006 highlighting the common association with Andean magmas. HFSE Sc versus transition-metal Ni marker for a mafic origin. b) Tectonomagmatic environment 1007 (Bowden et al., 1984). Diagram of K₂O/Yb versus Ta/Yb where the 1008 tectonomagmatic environment provides evidence from the discrimination 1009 diagrams of Bowden et al. (1984) reporting Yb (LREE). Lines divide subduction 1010 from nonsubduction settings and arrows point to MORB and within-plate granite 1011 (WPG) endmembers. The purple star indicating primordial mantle is from 1012 Bowden et al. (1984), which approximately divides ocean arcs from active 1013 continental margins; central Andes and volcanic arc basalts are also from that 1014 1015 study. Shoshonitic (SHO), CA, and tholeiitic (TH) series are shown to also be consistent with mobile major-element diagrams in the other figures. Vectors on 1016 the right-hand side indicate different factors that may affect the bulk-rock 1017 distribution. Literature samples are from Deruelle (1982), Matthews et al. (1994), 1018 1019 Naranjo (1992), Wittenbrink (1997), Matthews et al. (1999), Rosner (2003), and 1020 Mamani et al. (2010).

Figure 9 – Spatial distribution of Rc/Ra in northern Chile. The locations of volcanoes are shown with black triangles. Lascar and Lastarria are indicated by blue triangles with black centered dots. The symbols for different ranges of Rc/Ra values of fumarole samples are explained in the legend.

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Figure 10 – Derived equivalent lithostatic pressure model for ascending magmas. ³He/⁴He ratios corrected for atmospheric contamination (Rc/Ra) are associated with magma intrusion events at (a) Lascar and (b) Lastarria.

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Sample ID	Volcano	Long (deg.)	Lat (deg.)	Alt. (m)	Material
LRA1	Lastarria	25° 9'17.11"S	68°31'32.36"O	4992	Escoria Block
LRA2	Lastarria	25° 9'17.11"S	68°31'32.59"O	4992	Escoria Block
LRA3	Lastarria	25° 8'31.437''S	68° 31'47.579''O	4697	Pumice fragments
LRA4	Lastarria	25° 8'12.814''S	68° 32'7.793''O	4558	Pumice fragments
LAS1	Lascar	23° 18'46.605''S	67° 47'0.67''O	3919	Dome fragment
LAS2	Lascar	23° 18'45.09''S	67° 47'2.197''O	3925	Escoria Block
LAS3	Lascar	23° 18'59.843''S	67° 47'48.253''O	3890	Escoria Block

Table 1 – Sample description

^a Aguilera (2008)

^b Dome fragment emitted inside 1993 pyroclastic flow

Sample		LAS1	LAS2	LAS3	LRA2
Volcano		Lascar	Lascar	Lascar	Lastarria
Material		Dome fragment (1989)	Escoria Block	Escoria Block	Escoria Block
SiO ₂ (wt.%)	0.01	57.86	58.2	57.39	58.06
Al ₂ O ₃	0.01	16.75	16.17	16.04	16.88
Fe ₂ O ₃ (T)	0.01	7.11	7.62	7.49	7.36
MnO	0.001	0.124	0.123	0.125	0.114
MgO	0.01	4.39	4.26	4.61	4.22
CaO	0.01	7.17	7.18	7.2	6.74
Na ₂ O	0.01	3.36	3.49	3.39	3.34
K₂O	0.01	1.61	1.57	1.54	1.95
TiO ₂	0.001	0.724	0.821	0.776	0.979
P ₂ O ₅	0.01	0.18	0.31	0.24	0.21
LOI		n.d.	0.3	0.14	0.7
Total		99.21	100	98.95	100.6
Sc (ppm)	1	21	18	20	14
Ве	1	2	2	2	2
V	5	168	175	174	153
Ва	2	371	378	367	426
Sr	2	469	572	524	554
Y	1	19	20	19	15
Zr	2	127	142	135	177
Cr	20	110	100	90	170
Со	1	23	22	24	22
Ni	20	30	30	30	40
Cu	10	50	50	50	40
Zn	30	80	90	80	90
Ga	1	18	18	18	20
Ge	1	1	2	1	1
As	5	6	< 5	< 5	29
Rb	2	57	49	51	78
Nb	1	7	7	7	10
Мо	2	< 2	3	< 2	3
Ag	0.5	< 0.5	< 0.5	< 0.5	< 0.5
In	0.2	< 0.2	< 0.2	< 0.2	< 0.2
Sn	1	2	2	1	2
Sb	0.5		0.9	1	2
Cs	0.5	3.5	2.8	3	5.1
La	0.1	19.5	22.9	20.7	29
Ce Dr	0.1	40.3	46.8	43.1	60
Pr Nd	0.05	4.74	5./1	5.2	7.04
ina	0.1	19.2	22.7	20.5	26.5

Table 2 – Chemical compositions of bulk rock

Region	Locality	Lat.	Long.	Sample type	R/Ra	⁴ He/ ²⁰ Ne	^₄ He ppm	²⁰ Ne ppm	Rc/Ra	Error +/-
Central Volcanic Zone	Lastarria CCVG3 lower fumarolic field	-25.154166	-68.523888	Dry gas samples fumaroles	5.34	176.76	10.80	0.06	5.35	0.048
Central Volcanic Zone	Lastarria CCVG2 lower fumarolic field	-25.154166	-68.523888	Dry gas samples fumaroles	5.27	157.37	9.61	0.06	5.28	0.050
Central Andes Volcanic Zone	Lastarria	-25.154166	-68.523888	Lower fumarole field		159.9			5.14	
Central Andes Volcanic Zone	Lastarria	-25.154166	-68.523888	Lower fumarole field		199.1			5.13	
Central Andes Volcanic Zone	Lastarria	-25.154166	-68.523888	Lower fumarole field		-			5.13	
AIR					1	0.318	5.24	16.48		

Table 3 – Chemical and isotopic compositions of noble gases from fumaroles.

Table 4 – Chemical and isotopic compositions of noble gases from fluid inclusions.

Sample ID	Period of volcanism	Mineral	Weight	⁴He	²⁰ Ne	⁴⁰ Ar	³⁶ Ar	R/Ra	⁴ He/ ²⁰ Ne	Rc/Ra	Error tot +/-	⁴⁰ Ar/ ³⁶ Ar Er	ror
			g	mol/g	mol/g	mol/g	mol/g					c	%

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APPENDIX9 Click here to download Background dataset for online publication only: APPENDIX_IX.xlsx

Declaration of interests

x The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: