Crustal controls on light noble gas isotope variability along the Andean Volcanic Arc

J. Lages1*, A.L. Rizzo2, A. Aiuppa1, A. Robidoux3, R. Aguilar4, F. Apaza4, P. Masias4

Abstract

This study combines new noble gas data from fluid inclusions in minerals from Sabancaya, Ubinas, and El Misti (CVZ, Peru) and Villarica (South Chile, SVZ) with a revised noble gas compilation in the Andes, to identify systematic along arc variations in helium isotope compositions. We find 3He/4He ratios varying from 0.8 RA (Colombia) to 7.4 RA (Ecuador) within the NVZ, and only as high as 6.4 RA in the CVZ (R0 is the atmospheric 3He/4He ratio of 1.39 × 10−6). These distinct isotope compositions cannot be explained by variable radiogenic 4He production via slab fluid transport of U and Th in the mantle wedge, since both NVZ and CVZ share similar slab sediment inputs (Th/La ∼ 0.08–0.13). Instead, the progressively more radiogenic 3He/4He signatures in Ecuador and Peru reflect 4He addition upon magma ascent/stage in the crust, this being especially thick in Peru (>70 km) and Ecuador (>50 km) relative to Colombia (~30–45 km). The intermediate compositions in the North (8.0 RA) and South (7.9 RA) Chile, both high sediment flux margins, mostly reflect a more efficient delivery of radiogenic He in the wedge from the subducted (U-Th-rich) terrigenous sediments. Our results bring strong evidence for the major role played by crustal processes in governing noble gas compositions along continental arcs.

Introduction

Subduction zones are the main drivers of volatile exchange between the Earth’s interior reservoirs and the atmosphere (Zellmer et al., 2015). Studying the chemical and isotopic imprints of arc-related fluids is key to resolve their origin and fate along convergent margins (Hilton et al., 2002). Noble gases in arc magmatic/hydrothermal fluids, and trapped as fluid inclusions (FIs) in minerals, are fundamental tracers of the relative contributions of potential sources at work in an arc context: the mantle, the subducted slab, and the arc crust (Sano and Fischer, 2013).

Poreda and Craig (1989) were among the first to investigate arc gas emissions for their noble gas isotope compositions. They reported 3He/4He ratios close to those found in MORBs (8 ± 1; Graham, 2002), implying a dominant helium origin from the mantle wedge above the subducted plate. However, Hilton et al. (2002) estimated an average of 5.4 Ra for volcanic arc gases globally. Lower than MORB 3He/4He ratios have been attributed to potential sources at work in an arc context: the mantle, the subducted slab, and the arc crust (Sano and Fischer, 2013).

This study combines new noble gas data from fluid inclusions in minerals from Sabancaya, Ubinas, and El Misti (CVZ, Peru) and Villarica (South Chile, SVZ) with a revised noble gas compilation in the Andes, to identify systematic along arc variations in helium isotope compositions. We find 3He/4He ratios varying from 0.8 RA (Colombia) to 7.4 RA (Ecuador) within the NVZ, and only as high as 6.4 RA in the CVZ (R0 is the atmospheric 3He/4He ratio of 1.39 × 10−6). These distinct isotope compositions cannot be explained by variable radiogenic 4He production via slab fluid transport of U and Th in the mantle wedge, since both NVZ and CVZ share similar slab sediment inputs (Th/La ∼ 0.08–0.13). Instead, the progressively more radiogenic 3He/4He signatures in Ecuador and Peru reflect 4He addition upon magma ascent/stage in the crust, this being especially thick in Peru (>70 km) and Ecuador (>50 km) relative to Colombia (~30–45 km). The intermediate compositions in the North (8.0 RA) and South (7.9 RA) Chile, both high sediment flux margins, mostly reflect a more efficient delivery of radiogenic He in the wedge from the subducted (U-Th-rich) terrigenous sediments. Our results bring strong evidence for the major role played by crustal processes in governing noble gas compositions along continental arcs.

Received 19 May 2021 | Accepted 22 October 2021 | Published 23 November 2021

1. Dipartimento DSTEaM, Università degli Studi di Palermo, Palermo, Italy
2. Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italy
3. Centro de Excelencia en Geotermia de los Andes (CEGA) y Departamento de Geología, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile
4. Instituto Geológico Minero y Metalúrgico, Observatorio Vulcanológico del INGEMMET, Arequipa, Peru

* Corresponding author (email: jonsanpedro.nogueiralages@unipa.it)
helium data, integrated with noble gas data from other volcanic zones in the Andes, are used to resolve crustal versus slab controls on noble gas isotope variability along the arc.

### Results

Our noble gas results derive from CO₂-dominated FIs trapped in olivine (Villarica, South Chile) and clinopyroxene (Peru) phenocrysts as gas (vapour) bubbles during and after magma crystallisation. The phenocrysts were handpicked from pyroclastic and scoria deposits at Villarica, and ballistic blocks and andesitic lava flows in Peru (Supplementary Information S-1). We focus on pyroxene in Peruvian volcanic products as, due to the more evolved nature of magmas produced along the CVZ, olivine is scarce and frequently found in insufficient amounts for noble gas analyses. We followed identical sample preparation and analytical procedures to those described in Lages et al. (2021) for bulk element and isotope composition measurements of noble gases in each sample.

Despite low helium concentrations in Peruvian phenocrysts (0.38–1.29 × 10⁻¹³ mol/g), we obtain consistent results for Sabancaya, Ubinas, and El Misti volcanoes. The maximum observed ³He/⁴He ratios range from 5.9 (±0.2) to 6.4 (±0.2) RA (Table S-1). As for Villarica, we measure similar helium concentrations in olivine (only as high as 1.27 × 10⁻¹⁵ mol/g). Both samples analysed yield comparable R₃/R₄ values (6.5 ± 0.1 and 6.7 ± 0.1; Table S-1), below the MORB range, yet significantly higher than that reported in Hilton et al. (1993) of 4.3 ± 0.8 RA.

### An Improved Catalogue for Light Noble Gases in Andean Fluids

Our new data (Table S-1) fill an information gap in the central and southern volcanic zones of the Andes and are interpreted in the context of a noble gas compilation (Table S-2) we assembled from published noble gas studies on quaternary volcanic centres along the arc.

In their global arc compilation, Hilton et al. (2002) listed 81 samples (predominantly <100 °C) with available ³He/⁴He information for the Andes (117 in Sano and Fischer, 2013). Our updated catalogue (Supplementary Information S-2) now includes a total of 261 gas samples, with a significantly higher representation of fluid inclusion data analysis. However, and despite the significant increase in the number of samples available (including for other noble gases such as Ar and Ne), the overall dataset remains predominantly dominated (>60 % of the total; Fig. 1) by low temperature (<100 °C) gas emissions. This reflects (i) the difficulty of accessing volcano summits where high temperature fumaroles are typically concentrated, and (ii) the widespread occurrence of more accessible, peripheral manifestations (bubbling springs, steaming grounds, diffuse degassing) in volcano surroundings. Unfortunately, these are recurrently affected by secondary processes, including dilution of “magmatic” fluids by atmospheric/ crustal He that ultimately lowers the pristine ³He/⁴He ratio (e.g., gas manifestations at 0–100 °C and >3 km distance from the volcanic centre exhibit the lowest ³He/⁴He ratios on average; Fig. 1).

To overcome these limitations, recent studies have focused on the analysis of olivine- and pyroxene-hosted FIs found in lavas and pyroclastic deposits from active Andean volcanoes lacking noble gas information (e.g., Robidoux et al., 2020). Consequently, our novel data reported here for Ubinas, El Misti, and Sabancaya (Peru, CVZ), where surface gases have traditionally been challenging to measure (due to high level of activity at the open vents), delivers the first characterisation of noble gas signatures in the region. These, alongside our new noble gas results for Villarica (SVZ), provide the most thorough analysis of helium isotope compositions along the Andean volcanic arc.

### Exploring the Catalogue: Surface Gases vs. Fluid Inclusions

Our updated Andean dataset (Table S-2) benefits from the significant addition of FIs data to a yet gas-dominated compilation. More importantly, it ensures significant representability of three Andean arc segments (NVZ, CVZ and SVZ), and especially of some of their current most active volcanoes. FIs account for only ~12 % of the helium dataset (Fig. 1). While Ne and Ar exhibit large proportions of atmospheric components, FIs generally exhibit higher ³He/⁴He ratios than surface gases. Figure 2 explores the ³He/⁴He populations of three Andean segments, and finds that (with the notable exception of Galeras; Sano et al., 1997) FIs yield higher R₃/R₄ values than surface gases. Therefore, although FIs can potentially be affected by post-entrapment ³He and ⁴He in growth and diffusion controlled isotope fractionation, their ³He/⁴He signatures offer the most faithful record of pristine magmatic source compositions. Our inferred magmatic end member compositions are shown in Figure 2, as derived from using the maximum R₃/R₄ values for each arc segment. These are used below to interpret variations of ³He/⁴He signature in the mantle source along the arc.

### Subducting Slab or Continental Crust?

Accepting our segment maximum R₃/R₄ values (Fig. 2) as the most representative of the Andean magmatic source(s) (e.e.,...
g., as those least affected by secondary processes), we find little evidence of radiogenic contributions in Colombia and North/South Chile, in which the magmatic end members yield MORB-like values. However, more radiogenic 3He/4He ratios are observed in Ecuador and Peru (Fig. 2). Our goal below is to address if the drivers of these along arc variations operate (i) deep in the mantle source (via the subducting slab), or (ii) in the crust during magma ascent/storage.

Slab sediments are known as effective U and Th carriers (e.g., Kelley et al., 2005), and the fluids/melts they form by dehydration/melting (Skora et al., 2015) may in principle lead to substantial radiogenic 4He production (with a consequent 3He/4He ratio decrease) in the overriding mantle (Robidoux et al., 2017). We test the possible role of recycled subducting sediments using the Th/La ratio slab proxy (Supplementary Information S-4; Plank, 2005). The ratio between these fluid-immobile elements is typically low in MORBs (<0.1), elevated in the continental crust (>0.25), and varies in arc basalts (∼0.1–0.4) depending on the composition of sediments subducted at the corresponding trenches.

Plank (2005) demonstrates, for margins with high sediment fluxes (>0.32 Mg/yr/cm length), a correlation between Th/La in arc rocks and subducting sediments at corresponding trench. North and South Chile are the only Andean margins that fall in the high sediment flux category (0.53 and 0.55 Mg/yr/cm length, respectively), and their rock/sediment Th/La association consistently plot along the global array of Plank (2005), suggesting effective transfer of sediment-derived fluids to arc magmas in these regions (Fig. 3a, Table S-3). By contrast, Colombia, Ecuador and Peru, all low flux segments, exhibit a large spread in bulk volcanic rock Th/La compositions and 3He/4He ratios, and no obvious correlation with sediment Th/La (Fig. 3a).

Instead, the Th/La vs. 3He/4He ratios association (Fig. 3b) is more consistent with the involvement of crustal fluids in the latter segments. We cannot exclude however, based on the results of Figure 3b, that the ∼1 Ra difference between Colombia (8.5 and 8.8 Ra) and North/South Chile (7.9 and 8.0 Ra, high Th/La ratios of ∼0.33 and 0.32, respectively; Fig. 3b; Tables S-3, S-4; Plank, 2014) is, at least partially, due to a higher U-Th slab recycling via subduction of sediments in the latter segment.

From Ballentine and Burnard (2002) the production rate of radiogenic 4He from U and Th decay in the mantle wedge can be calculated as:

\[
\text{4He atoms g}^{-1} \text{ yr}^{-1} = \left( 3.115 \times 10^8 + 1.272 \times 10^8 \right) \frac{[\text{U}]}{\text{C}^{138}} + 7.710 \times 10^7 \frac{[\text{Th}]}{\text{C}^{138}}
\]

where [U] and [Th] correspond to the abundance of these elements in terrigenous products subducted in the region (Plank, 2014; Table S-3). Additionally, we assume (i) mantle 4He concentrations in the same range of those measured in gas-rich fluid inclusions from Andean products (e.g., Ecuador; ×10^{-32} mol/g; Lages et al., 2021), and (ii) a mantle end member derived from the highest 3He/4He ratios measured in FIs (8.5 Ra, Nevado del Ruiz; Lages et al., 2021). From these, we estimate that in 10 kyr enough radiogenic 4He would be produced to lower the helium isotope signature of the underlying mantle wedge toward North/South Chile end member values. This estimate is similar to the time length of slab dehydration and mantle wedge contamination happening via sediment melts transported in the slab (Plank, 2005).

Figure 2 3He/4He vs 4He/20Ne data in FIs and free gases. Binary mixing (air-magmatic end member) curves calculated with maximum RC/RA values for each segment.

Figure 3 (a) Average Th/La in subducting sediments and volcanic arcs (Plank, 2005). For Andean segments, bulk sediment and arc compositions (Table S-3) are derived from Plank (2014) and the Andean GEOROC dataset, respectively (see Supplementary Information S-4). (b) 3He/4He averages and end members (this work) vs. bulk Th/La compositions of respective segments; the grey area indicates a binary mixing line between MORB and continental crust.
We next test the hypothesis of a primary crustal control on the observed along arc variations in $^{3}$He/$^{4}$He signatures, by matching these with the regional changes in crustal thickness (e.g., Assumpção et al., 2013; Fig. 4). On the south to north transect (Fig. 4), MORB-like helium isotope ratios are initially observed in North (CNV) and South Chile (SVZ; 8.0 and 7.9 R$_{A}$, respectively), where the crust is 45–50 km thick. In the Peruvian Central Volcanic Zone, the more radiogenic He signature corresponds to the area where the crust is the thickest (>70 km). In this sector, all $^{3}$He/$^{4}$He values obtained for Sabancaya, El Misti and Ubinas are <6.5 R$_{A}$ and show low inter-variability. In Ecuador, we find both an increase in $^{3}$He/$^{4}$He ratios (~7.4 R$_{A}$), and a decrease in crustal thickness (~50 km). The latter remains roughly constant up to the south of Colombia (~45 km), where in Galeras values as high as 8.8 R$_{A}$ in fumarolic gases were reported by Sano et al. (1997). However, further north, crustal thickness decreases to ~35 km below Nevado del Ruiz and olivine-hosted FIs record $^{3}$He/$^{4}$He values amongst the highest ever recorded in arc volcanism (8.5 R$_{A}$).

A co-variation between $^{3}$He/$^{4}$He signatures and crustal thickness shows significant correlation at the scale of the entire arc (see inset Fig. 4). From this, we propose that the addition of radiogenic crustal $^{4}$He to magma ascending through (being stored within) U-Th-rich crustal lithotypes are the main control factor on fluid $^{3}$He/$^{4}$He signatures of continental arc volcanoes (Fig. 4). The unequivocal correlation we bring to light for most of the Andes further underlines the sensitivity of He isotopes in identifying and assessing crustal contamination processes. This correlation must be tested at arc scale in other subduction zones globally, as a more relevant role of the slab can be anticipated in regions where terrigenous sediments dominate the sedimentary input.

Acknowledgments

Two reviewers substantially improved this paper and are gratefully acknowledged. We thank Marco Rivera (OVI-INGEMMET) for his support during fieldwork in Peru and Aaron Sancho for his work on Challupén samples (Villarica). INGV-Palermo provided the analytical facilities. We thank Mariano Tantillo and Mariagrazia Misseri for their support in sample preparation and noble gas analysis. The fieldwork portion of this work was funded by the DECADE initiative, from the Deep Carbon Observatory – Alfred P. Sloan Foundation. This study also received funding from Miur under grant PRIN2017-2017LMNLAW.

Editor: Maud Boyet

Additional Information


References


Our work was supported by the DECADE initiative, from the Deep Carbon Observatory – Alfred P. Sloan Foundation. This study was also received funding from Miur under grant PRIN2017-2017LMNLAW.


Crustal controls on isotope variability of light noble gases along the Andean Volcanic Arc

J. Lages, A.L. Rizzo, A. Aiuppa, P. Robidoux, R. Aguilar, F. Apaza, P. Masias

Supplementary Information

The Supplementary Information includes:

- **S-1** New Isotope Results and Noble Gas Abundances (Peru and Chile)
  - Brief Petrological Descriptions of Volcanoes Sampled in This Study
  - Table S-1
- **S-2** Data References, Dataset Description and Full Data Table (with Table Guide)
  - S-2.1 Catalogue References
  - S-2.2 Table Guidelines
  - Table S-2
- **S-3** Neon and Argon Systematics of Andean Magmatic Fluids
  - Figures S-1 and S-2
- **S-4** Slab Constraints from Th/La in Sediments (Subducted) and Volcanic Products (Erupted) Along the Andean Volcanic Arc
  - Tables S-3 and S-4
- Supplementary Information References
S-1 New Isotope Results and Noble Gas Abundances (Peru and S Chile)

Brief Petrological Descriptions of Volcanoes Sampled in This Study

Sabancaya (Peru, CVZ)

The Ampato–Sabancaya volcanic complex comprises two successive edifices. During the Holocene, eruptive activity migrated to the NE and built up the Sabancaya edifice, between 6 and 3 ka. This cone comprises andesitic and dacitic blocky lava flows emplaced during at least two eruptive stages (Samaniego et al., 2016). The Ampato–Sabancaya rocks display a high-K magmatic affinity and range from andesites to dacites (57–69 wt. % SiO₂), with rare rhyolitic compositions (74–77 wt. % SiO₂). We analysed two lava samples from the Sabancaya basal edifice (3 ± 5 ka; Samaniego et al., 2016) that present porphyritic texture, composed of phenocrysts (30–60 vol. %) of plagioclase, biotite, amphibole, clinopyroxene, Fe-Ti oxides, and eventually by orthopyroxene and olivine (<2 %; Samaniego et al., 2016). The FIs analysed from noble gases in this study were entrapped in clinopyroxene host minerals (Table S-1).

Ubinas (Peru, CVZ)

Over the past 500 years, Ubinas produced mostly tephra with a trend towards more mafic magma compositions in recent times (Thouret et al., 2005). The 2006 and 2014 juvenile blocks here analysed are dark to grey, dense to poorly vesicular, porphyritic andesites bearing 20–25 vol. % phenocrysts (300 μm to 1.8 mm), 30–40 vol. % microphenocrysts (100–300 μm), and 35–50 vol. % matrix glass. Phenocrysts of plagioclase, clinopyroxene, orthopyroxene, and Fe-Ti oxides are abundant. Both samples show a similar mineral assemblage including plagioclase, clinopyroxene, orthopyroxene, and magnetite with scarce amphibole and olivine (Rivera et al., 2014). Olivine phenocrysts occur in the 2006 ballistic blocks, although not in sufficient amounts for FIs analysis of noble gases.

El Misti (Peru, CVZ)

El Misti is a major andesitic volcano located near the city of Arequipa in the northern Central Volcanic Zone. Plagioclase is by far the most abundant mineral phase followed in order of abundance by amphibole and pyroxene. Olivine occurs only in mafic andesites and when present is scarce, never exceeding 2 vol. %. Rivera et al. (2017) report on subhedral to anhedral olivine crystals with sizes smaller than 400 μm for Misti 2 lava flows from which both samples in this study were collected (112–40 ka), with forsterite composition of Fo76–80. When compared with olivines from primitive arc magmas (Fo80), the relatively low-Fo content of the El Misti olivine (Fo70–80) provides evidence against a pure, primary, mantled-derived origin for El Misti rocks (Rivera et al., 2017).

Villarrica (CSVZ, South Chile)

Activity at Villarrica has been characterised in the past by frequent small eruptions as well as highly explosive, caldera-forming pyroclastic eruptions of mainly basaltic andesite magma (Moreno and Clavero, 2006). Samples collected for analysis included scoria samples from the 3 March 2015 paroxysmal eruption (Aiuppa et al., 2017), with Fo contents ranging from about 70 to 82 % (avg. 77 %). Previously analysed samples representing the magma filling the central crater were determined to hold 33 wt. % plagioclase (An38–74), 7 wt. % olivine (Fo75–78), and trace amounts of chromian spinel (Witter et al., 2004). The other sample analysed (HCH2A1; Sancho, 2019) is taken from a ~100-m-high adventitious eruptive centre from the sub-group 2 of Chaillupén hch2 (<3.7 ka; Moreno and Clavero, 2006). The rock represents a ballistic projectile taken on the crater rim of a pyroclastic cone, ubicicated downhill at the southern end of the N–S fracture that cuts through Villarrica’s south flank. The rock sample is characterised as a fine-grained, dense fusiform bomb-size pyroclast of mafic composition with 20 vol. % plagioclase, 6 vol. % clinopyroxene, 4 vol. % olivine as determined from thin section analysis.
Table S-1  Noble gas abundances and isotope compositions in fluid inclusions (Peru and S Chile).

<table>
<thead>
<tr>
<th>Volcano</th>
<th>Sample ID</th>
<th>Sample details</th>
<th>Rock</th>
<th>Min. phase</th>
<th>$[\text{He}]_{\times 10^{13}}$</th>
<th>$[\text{Ne}]_{\times 10^{17}}$</th>
<th>$[\text{36Ar}]_{\times 10^{12}}$</th>
<th>$[\text{40Ar}]_{\times 10^{15}}$</th>
<th>$[\text{40Ar}^*]_{\times 10^{13}}$</th>
<th>$4\text{He}/20\text{Ne}$</th>
<th>$20\text{Ne}/22\text{Ne}$</th>
<th>$21\text{Ne}/22\text{Ne}$</th>
<th>$4\text{He}/40\text{Ar}$*</th>
<th>$40\text{Ar}/36\text{Ar}$</th>
<th>$3\text{He}/4\text{He}(\text{R}/\text{A})$</th>
<th>$3\text{He}/4\text{He}(\text{R}/\text{C}/\text{R}/\text{A})$</th>
<th>$\text{CO}_2/3\text{He}$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>South Chile (SVZ)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Villarrica</td>
<td>2015_B</td>
<td>Scoria</td>
<td>BA</td>
<td>Ol</td>
<td>1.27</td>
<td>2.50</td>
<td>6.15</td>
<td>20.38</td>
<td>1.24</td>
<td>50.8</td>
<td>9.83 ± 0.03</td>
<td>0.0295 ± 0.0005</td>
<td>1.02</td>
<td>301.6 ± 0.1</td>
<td>6.43</td>
<td>6.46 ± 0.12</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCH2A1</td>
<td>Pyroclast (bomb)</td>
<td>BA</td>
<td>Ol</td>
<td>0.72</td>
<td>10.32</td>
<td>1.03</td>
<td>3.40</td>
<td>0.21</td>
<td>7.0</td>
<td>9.81 ± 0.02</td>
<td>0.0293 ± 0.0003</td>
<td>3.39</td>
<td>301.8 ± 0.7</td>
<td>6.39</td>
<td>6.66 ± 0.13</td>
<td>0.627</td>
<td></td>
</tr>
<tr>
<td><strong>Peru (CVZ)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ubinas</td>
<td>2014</td>
<td>Juvenile blocks</td>
<td>A</td>
<td>Cpx</td>
<td>0.72</td>
<td>9.86</td>
<td>6.95</td>
<td>19.75</td>
<td>11.19</td>
<td>7.3</td>
<td>9.67 ± 0.02</td>
<td>0.0284 ± 0.0003</td>
<td>0.06</td>
<td>352.2 ± 0.8</td>
<td>5.64</td>
<td>5.86 ± 0.16</td>
<td>16.461</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2016 A &amp; B</td>
<td>Juvenile blocks</td>
<td>A</td>
<td>Cpx</td>
<td>1.29</td>
<td>39.69</td>
<td>15.27</td>
<td>48.72</td>
<td>8.75</td>
<td>3.2</td>
<td>9.66 ± 0.02</td>
<td>0.0285 ± 0.0002</td>
<td>0.15</td>
<td>313.5 ± 0.04</td>
<td>5.49</td>
<td>6.01 ± 0.16</td>
<td>7.203</td>
<td></td>
</tr>
<tr>
<td>Sabancaya</td>
<td>SA-09-11</td>
<td>Lava flow</td>
<td>A</td>
<td>Cpx</td>
<td>0.38</td>
<td>10.63</td>
<td>0.71</td>
<td>1.98</td>
<td>1.27</td>
<td>3.6</td>
<td>9.67 ± 0.03</td>
<td>0.0288 ± 0.0004</td>
<td>0.30</td>
<td>359.7 ± 0.2</td>
<td>5.45</td>
<td>5.92 ± 0.23</td>
<td>0.484</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SA-09-17</td>
<td>Lava flow</td>
<td>A</td>
<td>Cpx</td>
<td>0.08</td>
<td>12.57</td>
<td>0.93</td>
<td>2.92</td>
<td>0.70</td>
<td>0.7</td>
<td>9.77 ± 0.01</td>
<td>0.0292 ± 0.0003</td>
<td>0.12</td>
<td>319.4 ± 0.1</td>
<td>1.45</td>
<td>2.11 ± 0.18</td>
<td>16.460</td>
<td></td>
</tr>
<tr>
<td>El Misti</td>
<td>Misti 2 (A)</td>
<td>Lava flow</td>
<td>A</td>
<td>Cpx</td>
<td>1.19</td>
<td>2.18</td>
<td>4.16</td>
<td>1.35</td>
<td>1.82</td>
<td>0.9</td>
<td>9.89 ± 0.01</td>
<td>0.0289 ± 0.0031</td>
<td>0.08</td>
<td>309.0 ± 0.06</td>
<td>3.93</td>
<td>5.80 ± 0.177</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Misti 2 (B)</td>
<td>Lava flow</td>
<td>A</td>
<td>Cpx</td>
<td>0.78</td>
<td>1.31</td>
<td>4.84</td>
<td>1.56</td>
<td>2.32</td>
<td>0.9</td>
<td>9.84 ± 0.01</td>
<td>0.0297 ± 0.00019</td>
<td>0.12</td>
<td>310.4 ± 0.06</td>
<td>4.43</td>
<td>6.36 ± 0.190</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

\* Host rock chemical classification on the basis of SiO$_2$ content: A, andesite; BA, basaltic-andesite.

b Mineral phases analysed: Ol, olivine; Cpx, clinopyroxene.

c Noble gas and CO$_2$ concentrations in mol g$^{-3}$. 
S-2 Data References, Dataset Description, and Full Data Table (with Table Guide)

The data table below includes He, Ar, and Ne data available for quaternary volcanoes from the Andean Volcanic Arc. Noble gas data reported for amagmatic regions of the arc (e.g., flat-slab segments) have not been included (see Simmons et al., 1987; Hoke et al., 1994; Hoke and Lamb, 2007; Newell et al., 2015).

S-2.1 Catalogue References (in Table S-2)


S-2.2 Table Guidelines

The colours of the headlines throughout the noble gas catalogue table correspond to the colour scheme used in the figures to distinguish between the five different countries and their respective volcanic arc segments (NVZ, Colombia and Ecuador; CVZ, Peru and North Chile; SVZ, South Chile):

i) Lat and Long columns: “Lat” (latitude) and “Long” (longitude), when not provided, were estimated by name of sampling location and/or map figures showing sampling coordinates; values inferred appear in red in both columns. Note that FIs data are assigned the exact coordinates of the volcanic edifice of origin.

ii) Dist. (m) and Temp. (°C): Values for distance (Dist.) and temperature (Temp.), when not originally reported, were assigned based on sampling coordinates (for distance to the main volcanic centre) and previous temperatures reported for the same sampling location (for the temperature column), all in red. Samples with no temperature and/or distance information are due to insufficient information available to infer the sampling parameters. For hydrothermal samples not associated with a main volcanic system, the distance parameter results non-applicable (n/a).

iii) Type: The dataset is subdivided into the following sample types (see also Fig. 1 in the main text): 1, fluid inclusions (FIs) data in olivine phenocrysts; 2, FIs in clinopyroxene; 3, FIs in orthopyroxene; 4, free gases at >100 °C; 5, free gases at 50–100 °C; 6, free gases at <50 °C.

iv) Isotope ratios correction: Helium isotopic ratios reported in the form of $R_C/R_A$, where $R_C$ is the air-corrected $^3\text{He}/^4\text{He}$ ratio of the sample, assessed based on $^4\text{He}/^20\text{Ne}$ ratios (also in table):

$$R_C/R_A = [(R_M/R_A)(\text{He/Ne})_M - (\text{He/Ne})_{\text{air}}]/[(\text{He/Ne})_M - (\text{He/Ne})_{\text{air}}],$$

where the subscripts “M” and “air” refer to measured and atmospheric theoretical values, respectively. Argon isotope ratios account for atmospheric-corrected $^4\text{Ar}$, assuming that all $^36\text{Ar}$ contained in the gas phase is of atmospheric origin:

$$^4\text{Ar}^* = ^4\text{Ar}_M - [^{40}\text{Ar}/^{36}\text{Ar}]_{\text{air}}\times^{36}\text{Ar}_M,$$

where $^{40}\text{Ar}^*$ represents the corrected isotope value and M indicates the measured value.

v) err: Isotopic ratio errors are 1σ uncertainties.

Table S-2 Noble gas catalogue of the Andean Volcanic Arc.

Table S-2 is available for download (Excel) from the online version of the article at http://www.geochemicalperspectivesletters.org/article2134.
S-3 Neon and Argon Systematics of Andean Magmatic Fluids

In contrast to the extensive $^3$He/$^4$He database described in the main text, there are relatively few $^{40}$Ar/$^{36}$Ar samples (118) and even fewer $^{20}$Ne/$^{22}$Ne and $^{21}$Ne/$^{22}$Ne samples (34 and 33, respectively; Fig. S-1).

Compared to intraplate and middle oceanic ridge environments, subduction-related fluids are known to carry larger proportions of atmospheric components (Burnard et al., 1997), and Ar isotopes in FIs from volcanic arc rocks consistently show $^{40}$Ar/$^{36}$Ar ratios close to the atmosphere (295.5; Hilton et al., 2002). In our catalogue, the observed Andean gas-rocks $^{40}$Ar/$^{36}$Ar ratios range from 287.5 to 610, but the arc average of ~339 (taken across all gas-rocks samples) denotes a close-to-atmospheric $^{40}$Ar/$^{36}$Ar signature, well below that of MORB (~44,000; Moreira et al., 1998). Similarly, neon isotopes ($\leq$0.038 for $^{21}$Ne/$^{22}$Ne and $\leq$10.46 for $^{20}$Ne/$^{22}$Ne) cluster at around the atmospheric ratios (0.029 and 9.8 for $^{21}$Ne/$^{22}$Ne and $^{20}$Ne/$^{22}$Ne, respectively; Sarda et al., 1988). These atmospheric Ar-Ne isotopic signatures imply variable (but substantial) degrees of contamination by an atmosphere-derived component that reflect their relatively large (compared to helium) air abundances (Hilton et al., 2002; Fig. S-2). Notably, FIs also exhibit this atmospheric imprint: their Ne isotopic pairs and $^{40}$Ar/$^{36}$Ar ratios (see histogram in Figs. 1 and S-1) are often lower than in high-temperature gases and comparable to those obtained from low-temperature emission sources. Recycling of atmosphere-derived Ar in the mantle, via dehydration of the subducting oceanic crust, has often been invoked (Matsumoto et al., 2001; Hopp and Ionov, 2011; Di Piazza et al., 2015; Rizzo et al., 2016; Robidoux et al., 2017, 2020; Battaglia et al., 2018), although air contamination during surface rock exposure is often difficult to rule out.

Figure S-2 illustrates the binary trends of atmosphere-mantle mixing for both Argon and Neon isotopic ratios. Most importantly, our dataset indicates that atmosphere-derived components are still dominant even in FIs. Contrarily to the $^3$He/$^4$He results, these show little difference when compared to argon and neon isotope results obtained in free gases, including those <100 °C (see Fig. 1 in the main text).
S-4 Slab Constraints from Th/La in Sediments (Subducted) and Volcanic Products (Erupted) Along the Andean Volcanic Arc

To test the possible slab control on the $^{3}$He/$^{4}$He signature of the mantle wedge along the Andes, we followed the approach of Plank (2005), who used the Th/La ratio as a tracer for the contribution of subducting sediments to arc magmas. This tracer is particularly useful since radiogenic $^{4}$He mostly derives from the decay of natural U and Th series elements in rocks and sediments.

The author suggests that where little sediment subducts, arcs should have approximately mantle Th/La, whereas, in places with a high flux of subducted sediment, the Th/La of the arc should approach the sediment ratio. The latter varies with the proportions of terrigenous, hydrogenous and volcaniclastic sources. Th/La signatures in arc magmas should therefore provide information on the proportion of sediment to mantle, and therefore a way to calibrate the influence of sediment melts delivered by the slab at an arc-segment scale.

The Th/La data used in Figure 3a, b (main text) have been extracted from the ‘GEOROC’ (Geochemistry of Rocks of the Oceans and Continents) database (http://georoc.mpch-mainz.gwdg.de/georoc/Start.asp). The relevant data have been taken from the ‘Precompiled Files/Locations/Convergent Margins’ files ‘ANDEAN ARC part1.csv’ and ‘ANDEAN ARC part2.csv’ that are freely available for download. The following tables summarise the available dataset.
Table S-3  Th/La data used in Figure 3a.

<table>
<thead>
<tr>
<th>Arc Segment</th>
<th>Bulk Arc Segment Th/La (avg.)</th>
<th>1σ</th>
<th>Th/La</th>
<th>Th [ppm]</th>
<th>La [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colombia</td>
<td>0.1007</td>
<td>0.0383</td>
<td>0.083</td>
<td>1.21</td>
<td>14.6</td>
</tr>
<tr>
<td>Ecuador</td>
<td>0.1746</td>
<td>0.0464</td>
<td>0.083</td>
<td>1.21</td>
<td>14.6</td>
</tr>
<tr>
<td>Peru</td>
<td>0.1723</td>
<td>0.1084</td>
<td>0.124</td>
<td>3.54</td>
<td>28.6</td>
</tr>
<tr>
<td>N Chile</td>
<td>0.2399</td>
<td>0.1133</td>
<td>0.332</td>
<td>5.08</td>
<td>15.3</td>
</tr>
<tr>
<td>S Chile</td>
<td>0.2177</td>
<td>0.1081</td>
<td>0.318</td>
<td>4.74</td>
<td>14.9</td>
</tr>
</tbody>
</table>

* Including only samples with <58 wt. % SiO₂.

Table S-4  Th/La data used in Figure 3b.

<table>
<thead>
<tr>
<th>Volcanic system</th>
<th>GEOROC dataset</th>
<th>This review</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg Th/La of volcanic products</td>
<td>1σ</td>
</tr>
<tr>
<td>Nevado del Ruiz</td>
<td>0.2665</td>
<td>0.0798</td>
</tr>
<tr>
<td>Galeras</td>
<td>0.2953</td>
<td>0.0684</td>
</tr>
<tr>
<td>Cotopaxi</td>
<td>0.3099</td>
<td>0.1552</td>
</tr>
<tr>
<td>Tungurahua</td>
<td>0.3262</td>
<td>0.1183</td>
</tr>
<tr>
<td>El Reventador</td>
<td>0.1584</td>
<td>0.0182</td>
</tr>
<tr>
<td>Ubinas</td>
<td>0.1800</td>
<td>0.0344</td>
</tr>
<tr>
<td>El Misti</td>
<td>0.3462</td>
<td>0.2109</td>
</tr>
<tr>
<td>Sabancaya</td>
<td>0.2432</td>
<td>0.1303</td>
</tr>
<tr>
<td>Lascar</td>
<td>0.3160</td>
<td>0.1087</td>
</tr>
<tr>
<td>Lastarria</td>
<td>0.5908</td>
<td>0.1473</td>
</tr>
<tr>
<td>Villarica</td>
<td>0.1956</td>
<td>0.0694</td>
</tr>
<tr>
<td>Copahue</td>
<td>0.4165</td>
<td>0.0001</td>
</tr>
</tbody>
</table>
Supplementary Information References


