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Letters

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

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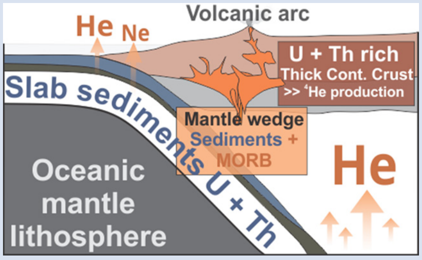
Abstract



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 8.8 R_A (Colombia) to 7.4 R_A (Ecuador) within the NVZ, and only as high as 6.4 R_A in the CVZ (R_A 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/storage 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 R_A) and South (7.9 R_A) 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.

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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 R_A for volcanic arc gases globally. Lower than MORB $^3He/^4He$ ratios have been explained invoking either (i) assimilation of ^4He-rich crustal fluids during magma crustal storage/ascent (*e.g.*, Mason *et al.*, 2017), or (ii) addition of radiogenic ^4He to the mantle wedge (Hanan and Graham, 1996) *via* subducted slab sediments (if U + Th-rich sediments are involved; Kagoshima *et al.*, 2015).

The Andean volcanic arc offers a unique opportunity to evaluate the crust *versus* slab hypotheses. The ~7000 km long arc is subdivided into four volcanic zones (VZs), three of which are investigated here (Northern VZ, Colombia and Ecuador; Central VZ, Peru and North Chile; and Southern VZ, South Chile). Ancellin *et al.* (2017) and Mamani *et al.* (2010) noted, for the Ecuadorian and Peruvian arcs, respectively, high degrees of crustal assimilation by magmas erupted in the region. Along the trench, the age of the subducted oceanic floor (46.2 Ma in North-Central Chile to 10.3 Ma in South Chile; Syracuse *et al.*, 2010) and the degree of obliquity of the subducted slab (similar across the active volcanic zones) are other key factors impacting magma genesis and distribution of active volcanism in the Andes (Stern, 2004). Moreover, slab contributions have been noted in the C content of volcanic gas emissions (Aiuppa et *al.*, 2017), whose compositions strongly correlate with the nature of subducted sediments in each region (Plank, 2014). However, in addition to the role of the slab, crustal processes have also been invoked (Hidalgo *et al.*, 2012), especially for noble gas compositions previously reported for the continental arc (*e.g.*, Hilton *et al.*, 1993).

Here, we present the very first noble gas data from Sabancaya, Ubinas, and El Misti (Central Volcanic Zone, Peru) and report on new noble gas chemical and isotope compositions for Villarica (South Chile). These were obtained from the analyses of bulk (primary and secondary) fluid inclusion compositions in minerals (olivine and pyroxene), which are key in providing noble gas compositions of the magmatic source, especially when surface emissions are absent or difficult to access. Our new

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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 CO_2-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 recurrently 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 ($0.38–1.29 \times 10^{-13}$ 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) R_A (Table S-1). As for Villarica, we measure similar helium concentrations in olivine (only as high as 1.27×10^{-13} mol/g). Both samples analysed yield comparable R_C/R_A 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 R_A.

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.

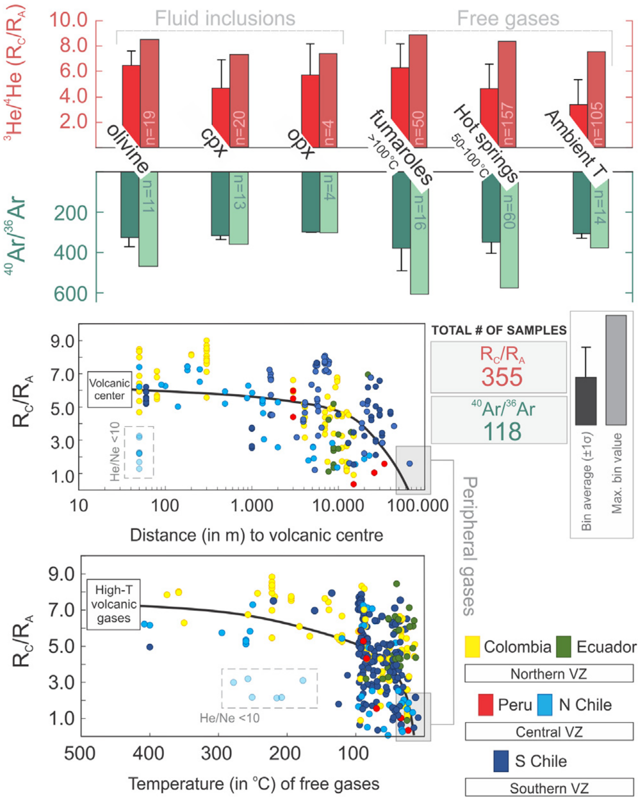

Figure 1 Distribution of helium and argon isotopic data (averages and maximum values) *per* sample category. Bottom: relation between R_C/R_A data in free gases, their sampling temperature, and distance to respective volcanic centres (Table S-2).

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 R/R_A 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 R_C/R_A 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 R_C/R_A values (Fig. 2) as the most representative of the Andean magmatic source(s) (*e.*

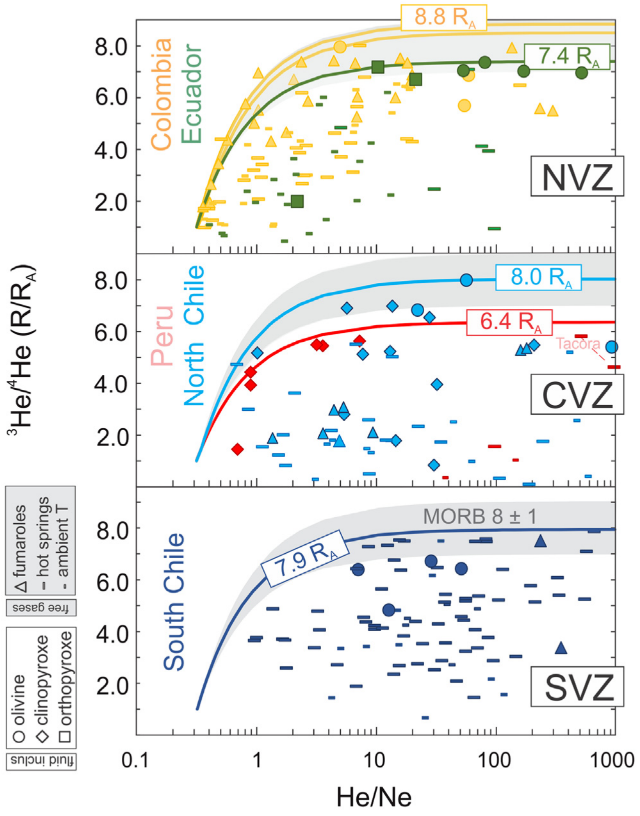

Figure 2 $^3He/^4He$ *vs* $^4He/^{20}Ne$ data in FIs and free gases. Binary mixing (air-magmatic end member) curves calculated with maximum R_C/R_A values for each segment.

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).

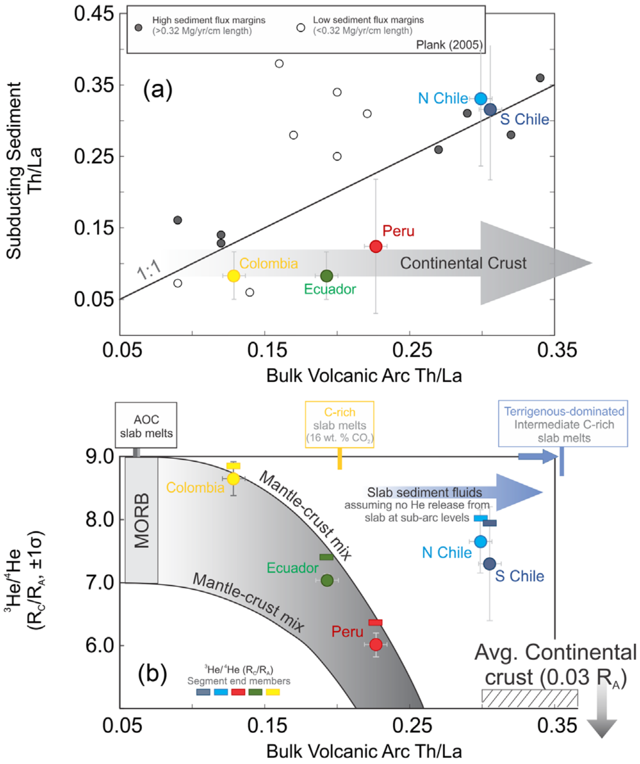

Figure 3 **(a)** Average Th/La in subducting sediments and volcanic arcs (Plank, 2005). For Andean segments, bulk sediment and arc compositions (Table S-3) are derived from Plank (2014) and the Andean GEOROC dataset, respectively (see Supplementary Information S-4). **(b)** $^3He/^4He$ averages and end members (this work) *vs*. bulk Th/La compositions of respective segments; the grey area indicates a binary mixing line between MORB and continental crust.

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 R_A difference between Colombia (8.5 and 8.8 R_A) and North/South Chile (7.9 and 8.0 R_A, 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:

$$^4\text{He atoms g}^{-1}\,\text{yr}^{-1} = (3.115 \times 10^6 + 1.272 \times 10^5)\,[\text{U}] + 7.710 \times 10^5\,[\text{Th}]$$

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^{-12} mol/g; Lages *et al.*, 2021), and (ii) a mantle end member derived from the highest $^3He/^4He$ ratios measured in FIs (8.5 R_A, 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).

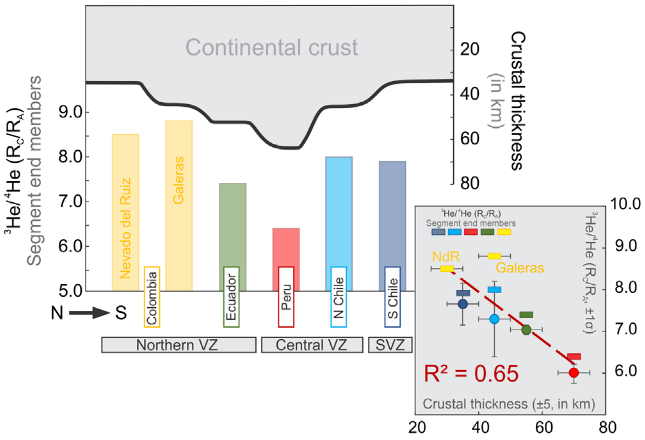

Figure 4 Crustal thickness variations along the Andes (transect); bottom, ^{3}He/^{4}He end members of respective arc segments (Fig. 2). Inset: co-variation of He isotopic signatures (avg. ±1σ, and end members) and crustal thicknesses at the arc scale; due to the crustal thickness anomaly detected at Nevado del Ruiz, the latter and Galeras are plotted separately.

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 (CVZ) and South Chile (SVZ; 8.0 and 7.9 R_A, respectively), where the crust is 45–30 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 subducting input.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2134.

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