Upper crustal differentiation processes and their role in 238U-230Th disequilibria at the San Pedro-Linzor volcanic chain (Central Andes)

Benigno Godoy*a, Lucy McGeeb,1, Osvaldo González-Maurelc,d, Inés Rodríguez*, Petrus le Rouxd, Diego Morataa, Andrew Menziesf

a Centro de Excelencia en Geotermia de los Andes (CEGA) y Departamento de Geología, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Plaza Ercilla 803, Santiago, Chile
b Department of Earth and Planetary Sciences, Macquarie University, Sydney, NSW, 2109, Australia
c Departamento de Ciencias Geológicas, Universidad Católica del Norte, Avda. Angamos, 0610, Antofagasta, Chile
d Department of Geological Sciences, University of Cape Town, Rondebosch, 7700, South Africa
e Departamento de Obras Civiles y Geología, Facultad de Ingeniería, Universidad Católica de Temuco, Rudecindo Ortega, 02950, Chile
f Bruker Nano GmbH, Am Studio 2D, Berlin 12489, Germany

ARTICLE INFO

Keywords:
U-series disequilibria
San Pedro – Linzor volcanic chain
238U excess
Subduction zone magmatism
Amphibole fractionation

ABSTRACT

U-series data are combined with major and trace element constraints to construct a detailed view of the magmatic system feeding the San Pedro-Linzor volcanic chain, aiding the understanding of how stratovolcanoes in extremely thick arc crust evolve. Lavas from the Quaternary San Pedro-Linzor volcanic chain (Central Andes) have (238U/230Th) ranging from 1.015 to 1.072, with 238U excess even in the less evolved (~57 wt% SiO2) analyzed lavas. Contrary to well-established trends between fluid mobile elements and 238U excess, (238U/232Th)0 shows no systematic correlation with ratios indicative of fluid-driven melting (e.g. Ba/Hf and K/La). Moreover, the inverse correlation between (238U/232Th) with the amount of slab-derived fluid and the oxidation state of the mantle below Central Andes, which decreases eastwards, suggests that the main control of the 238U excess is not associated with hydration of the mantle wedge. Changes in (238U/232Th)0 and (230Th/232Th)0 are observed with variations in SiO2 and CaO + Al2O3 contents, and 87Sr/86Sr and Dy/Dy* ratios of the lavas. These changes correspond to increasing (238U/232Th) with decreasing Dy/Dy* and CaO + Al2O3 ratios, which is attributed to changes in crystallization of mineralogical phases within magmatic chambers during differentiation. Also, 230Th in-growth is produced during stagnation within magmatic chambers located below the San Pedro-Linzor volcanic chain. Finally, a positive correlation between (238U/232Th)0 and 87Sr/86Sr indicates an important role of crustal contamination, and of new magmatic inputs during evolution of the volcanic chain with time. Our observations suggest that better constraints of all magmatic processes are needed to fully understand the U-series disequilibria recognized for the different volcanic structures developed within subduction-related tectonic environments.

1. Introduction

U-series disequilibria correspond to enrichment or depletion of daughter radionuclides (e.g. 230Th, 226Ra) relative to their radioactive parental isotope (e.g. 238U and 230Th respectively) over their respective half-lives. This disequilibrium may be related to a range of magmatic processes, such as the onset of fluid-flux melting, or the fractionation of a significant mineral phase, and can be used to constrain these processes, and dominate the timescales over which they occur (Condomines et al., 2003; Peate and Hawkesworth, 2005). In subduction-zones, the use of U-series disequilibria can establish the mantle characteristics of these tectonic environments, commonly associated with addition of slab-derived fluids and the in-growth of daughter isotopes through parental isotope decay (Turner et al., 2003; Huang et al., 2016). In these environments, the extent of disequilibria is also used to determine the different processes related to evolution and timescales of the mantle-generated magmas during their ascent (Condomines et al., 2003; Turner et al., 2003). Few magmas that erupt in arc environments, however, remain primitive due to crustal processing. To establish the behavior of U-series during mantle melting
processes it is therefore necessary to understand how the upper crustal processes affect the extent of this disequilibria.

The Central Andes corresponds to a subduction-related magmatic arc developed over a > 60 km thick continental crust (Beck et al., 1996). Primitive magmas at this arc are related to partial melting of peridotite mantle (Davidson et al., 1990; Burns et al., 2020) mainly by hydration from slab-derived fluids (Rosner et al., 2003; Araya-Vargas et al., 2019). However, the initial composition of the mantle-derived magmas is obscured by differentiation, mainly by crustal assimilation, occurring during their ascent to the surface (e.g. Davidson et al., 1990, 1991; Feeley and Davidson, 1994; Matthews et al., 1994; Garrison et al., 2006; Figueroa and Figueroa, 2006; de Silva and Kay, 2018; Burns et al., 2020; González-Maurel et al., 2020).

This work contrasts the effects of the different magmatic processes at upper crustal (< 40 km depth) levels in the control of U-series disequilibria in mantle-derived magmas at subduction-related environments. The main objective of this work is to understand how these processes influence the observed U-series disequilibria in young continental volcanic arcs. To establish this, we focus on the San Pedro-Linzor volcanic chain (Central Andes) using previous evolutionary models to discuss the roles of mineral fractionation and magmatic differentiation regimes in the genesis of this disequilibria. We selected samples from the least evolved products of this volcanic chain which were erupted in the last 270 kyr. These samples correspond to lava flows from Paniri and San Pedro volcano, and the lava flow and the scoria cone that form La Poruña.

2. Geological background

2.1. Main features of the San Pedro-Linzor volcanic chain

The San Pedro-Linzor volcanic chain (21°53′S 68°23′W - 22°09′S 67°58′W) corresponds to a ~65 km long NW-SE trending lineament of volcanic structures which were erupted in the western margin of the Altiplano-Puna Volcanic Complex (sensu de Silva, 1989) (Fig. 1). This volcanic chain was built in the last 2 Myr (Godoy et al., 2017), over an exceptionally thick continental crust (> 60 km, Beck et al., 1996), overlying Miocene ignimbrites and sedimentary sequences (Godoy et al., 2017; Selles and Gardeweg, 2017). The San Pedro-Linzor volcanic chain includes a series of different volcanic products such as lava flows and scoria fragments, which form mainly scoria cones (e.g. La Poruña), stratovolcanoes (e.g. San Pedro and Paniri), and coulee flows (e.g. Chao Dacite) (Fig. 1).

The volcanic products selected for this work correspond to different evolutionary stages of San Pedro and Paniri volcanoes, and from La Poruña scoria cone (Fig. 1). These structures were constructed separately (< 270 ka) (Fig. 1) (Godoy et al., 2018; González-Maurel et al., 2019a). Following the age criteria from González-Maurel et al. (2019a), samples from San Pedro were divided in Old (> 96 ka) and Young (< 96 ka) stages, whilst samples from Paniri correspond to Laguna (165–250 ka) and Llareta (100–165 ka) units from the New Cone Stage (Godoy et al., 2018). La Poruña represents in turn a short-lived eruption that occurred ca. 100 ka (González-Maurel et al., 2019a). Due to the importance of dating to U-series systematics, age information is discussed in detail in section 3 and summarized in Table S3.

2.2. Petrologic evolution of selected volcanic structures

Geochemical and isotopic characteristics indicate that the upper crustal magmatic evolution of the San Pedro-Linzor volcanic chain is associated, first, to the interaction of primitive magmas with partially molten layers of the crust distributed between 10 and 40 km depth (O’Callaghan and Francis, 1986; Godoy et al., 2014, 2017; González-Maurel et al., 2019b). This is similar to what is recognized in other Central Andean volcanoes (e.g. Davidson et al., 1990; Feeley et al., 1993; Matthews et al., 1994; Taussi et al., 2019), for which the
primitive magmas correspond to mantle-derived melts (e.g. Davidson et al., 1990; González-Maurel et al., 2019a, 2020; Burns et al., 2020) that ascend by exploiting crustal weaknesses (Feeley et al., 1993; Matthews et al., 1994; Figueroa and Figueroa, 2006; Taussi et al., 2019). In detail, a FC (fractional crystallization) process is recognized in the youngest stage of San Pedro volcano (i.e. San Pedro Young; González-Maurel et al., 2019a), whilst an AFC process is observed at the youngest stages of Paniri volcano (Godoy et al., 2018) (Fig. 2). Moreover, evolution in these shallow crustal magma chambers also includes small degrees of new inputs of primitive magmas (i.e. recharge), which decreases the Sr-isotope content of the erupted products (Godoy et al., 2018; González-Maurel et al., 2019a). This recharge is recognized in the youngest products of Paniri volcano and during the Old stage of San Pedro volcano (Fig. 2), and is also proposed for other volcanoes of the Altiplano-Puna Volcanic Complex (Feeley et al., 1993; Matthews et al., 1994). Finally, differentiation processes are suggested to occur with no magma stagnation (i.e. bypassing the Altiplano-Puna Magma Body; González-Maurel et al., 2019b). This is associated with selective contamination of primitive magmas during their ascent (i.e. assimilation during turbulent ascent-ATA; Huppert and Sparks, 1985). This process is associated with crustal contamination decreasing with increasing differentiation (i.e. silica content) as recognized at La Poruña and the oldest stage of evolution of San Pedro volcano (González-Maurel et al., 2019a) (Fig. 2), as well as for other Central Andean volcanic structures (Maro et al., 2017).

3. Methods

Major and trace elements, and Sr- and Nd-isotopic analysis, and results, were previously published (Godoy et al., 2014, 2018; González-Maurel et al., 2019a). This data is presented as Supplementary Material (Table S1). Full description of analytical methods, procedures, and results and errors of duplicate and standards analysis is given in González-Maurel et al. (2019a,b).

U and Th concentrations and activity ratios (denoted by parentheses; Table S2) were determined on bulk rock powders at the Macquarie University GeoAnalytical facility (MQGA). Approximately 0.3 g of powdered rock was spiked with a 236U–229Th tracer solution and digested in a mixture of concentrated acids (HF-HNO3) in Teflon beakers at 120 °C for 48 h. After digestion and dilution of the resultant solutions, U and Th were extracted from the rock matrix using 4 ml of a 5% HNO3 solution, and a linear tail correction U and Th isotope ratios were measured separately on a Nu Instrument Multi-Collector ICP-MS at Macquarie University. For U analyses, the New Brunswick Laboratory (NBL) synthetic standards U010 and U005a were used at regular intervals to assess the robustness of instrumental corrections and to monitor drift. For Th analyses, a standard-sample bracketing procedure for each sample analyzed used the Th ‘U’ standard solution, and a linear tail correction for the 232Th tail on 230Th was applied. Two samples (POR-15-05 and
SPSP-14-01) were duplicated as separate digestions and show good reproducibility in U and Th concentrations and activity ratios (see Table S2). Two separate digestions of TML (Table Mountain Latite) and one digestion of the USGS standard BCR-2 were prepared and analyzed at the same time as the samples. TML (average of the two analyses) was measured as \((^{230}\text{Th}/^{232}\text{Th}) = 1.073 \pm 0.006\), and \((^{238}\text{U}/^{232}\text{Th}) = 1.070 \pm 0.017\) which are within error of values reported by Scott et al. (2019) \((^{230}\text{Th}/^{232}\text{Th}) = 1.077 \pm 0.006\), \((^{238}\text{U}/^{232}\text{Th}) = 1.070 \pm 0.045\). BCR-2 was measured as \((^{238}\text{U}/^{232}\text{Th}) = 0.872 \pm 0.005\), and \((^{238}\text{U}/^{232}\text{Th}) = 0.878 \pm 0.014\) [Scott et al. (2019): \((^{230}\text{Th}/^{232}\text{Th}) = 0.879 \pm 0.005\), \((^{238}\text{U}/^{232}\text{Th}) = 0.877 \pm 0.015\)]. All standard and duplicate data and error are shown in Table S3.

As the lavas are all older than one half-life of \(^{230}\text{Th}\) ({75 ka}), previously published ages are used for isotopic corrections of \((^{230}\text{Th}/^{232}\text{Th})\) (given as \((^{230}\text{Th}/^{232}\text{Th})_0\) (see Table S2 and Fig. 1 for ages and dating method, and Table S4 for ages and parameters used for chronology calculations). La Poruña is a monogenetic scoria cone for which ages and dating method, andTable S4 for ages and parameters used for magmatic evolution of this volcanic structure (González-Maurel et al., 2019a). Sample SPSP-14-06 corresponds to the only analyzed lava from San Pedro without geochronological data which is located stratigraphically over the lava flow where sample SPSP-16-08 was collected (140 ± 40 ka) and below where sample SPSP-14-01 was obtained (60 ± 6 ka) (Fig. 1). Considering this sample corresponds to the younger (< 96 ka) lava suite of San Pedro (i.e. San Pedro Young; González-Maurel et al., 2019a), an age of 90 ka was used to correct the obtained \((^{230}\text{Th}/^{232}\text{Th})\) of this sample with an age range between 54 and 180 ka (Table S4). For sample PANI-16-02 from Paniri, an obtained age of 264 ± 99 ka has been published (Godoy et al., 2018). Stratigraphically, this sample corresponds to the Llareta Unit that was erupted between 100 and 165 ka (Godoy et al., 2018), therefore an age of 165 ka was used to correct the \((^{230}\text{Th}/^{232}\text{Th})\) data, and minimum and maximum ages of 165 and 264 ka were used as errors for this sample considering the obtained geochronological data (Fig. 1). For sample PANI-16-03, which corresponds to the only sample from Paniri without geochronological data, a correction age of 100 ka and an error range between 100 and 174 ka were used, as this sample is considered to be the youngest erupted product from Paniri volcano (Godoy et al., 2018).

4. Results

4.1. Petrographic characteristics

A brief review of the petrographic features of analyzed units is shown in Fig. 3. The mineralogical assemblage of the samples of La Poruña (Fig. 3a–b) consists of phenocrysts (10–30 vol%) of plagioclase, olivine, orthopyroxene and clinopyroxene, with minor amphibole, magnetite and ilmenite. The groundmass is composed of glass, with variable amounts of microlites of the same mineralogical phases of the phenocrysts. As for other Andean volcanoes (e.g. Bourdon et al., 2000; Garrison et al., 2006; Kiebala, 2008) the variation in \(^{238}\text{U}/^{232}\text{Th}\) disequilibria from the structures of the San Pedro-Linzor volcanic chain reflects either initial source melting processes or subsequent differentiation processes (Turner et al., 2003; Garrison et al., 2006; Huang et al., 2016). At subduction-related environments, mainly at oceanic arcs, \(^{238}\text{U}\) excesses are typically attributed to addition of fluids from the slab to the mantle wedge (Hawkesworth et al., 1997; Turner et al., 2003). This can be constrained with fluid-mobile trace elements (e.g. Ba and K) as indicated by El Misti volcano at the Central Andes (Kiebala, 2008), and the High-Mg basaltic center San Jorge in the Andean Southern Volcanic Zone (McGee et al., 2019). The basalts from San Jorge have large U-excesses and Ra-excesses which correlate with Ba/HF and K/Na ratios.
Their Sr isotopic compositions are close to mantle values (0.7039, McGee et al., 2019) with no correlation with indices of differentiation, suggesting little to no crustal contribution. These values are therefore representative of a mantle-dominated magmatic system, and this data could be extrapolated towards a fluid-enriched trend in $^{238}\text{U}/^{232}\text{Th}$ vs $^{230}\text{Th}/^{232}\text{Th}$ (Fig. 4a). For El Misti, mantle-derived fluid addition has proposed to play a key role in its magmatic evolution (Kiebala, 2008), suggested by the proposed model for this volcanic structure (Fig. 4a). However, although we cannot rule out U-excess contributions from the mantle for the magmatic evolution of the San Pedro-Linzor volcanic chain, which could be higher than those for El Misti (Fig. 4a), we believe these are later largely overprinted by crustal processes, as we now discuss. The less evolved analyzed samples of the San Pedro-Linzor volcanic chain (i.e. La Poruña) have $^{238}\text{U}$ excess, and the highest Ba/Hf ratios of the volcanic chain. However, the obtained Ba/Hf ratios are lower than those from El Misti (Fig. 5a), and these ratios do not correlate with $^{238}\text{U}/^{230}\text{Th}$ (Fig. 5b), as expected if fluids are related to $^{238}\text{U}$ enrichment (McGee et al., 2019). Similar characteristics are observed for K/La ratios, which are lower than those from El Misti and do not correlate with $^{238}\text{U}/^{230}\text{Th}$ (Fig. 5c and d). Moreover, the increase in $^{238}\text{U}$ from La Poruña to Paniri is not correlated with the increasing of mantle hydration by slab-derived fluids in the same direction (Rosner et al., 2003) (Fig. 4b). This indicates that, even though fluid addition can be responsible for an initial $^{238}\text{U}$ excess, as observed for La Poruña, this is not the main process controlling this isotopic enrichment for the volcanic chain, as usually suggested for subduction-related volcanism (e.g. Turner et al., 2003; Garrison et al., 2006; Kiebala, 2008; Brens Jr., 2011; Huang et al., 2017; McGee et al., 2019).

$^{238}\text{U}$ excess can also be generated by in-growth melting processes in the mantle, which is generated by melting of a low porosity matrix (i.e. mantle-wedge) (Huang et al., 2011). This process occurs in an oxidized mantle wedge, as higher oxygen fugacity causes a decrease in $\text{D}_{\text{U}/\text{Th}}$ from $> 1$ to $< 1$ (Huang et al., 2011). Glocce et al. (2016) indicated that high oxygen fugacity exists for magmas erupted in the Central Andes, based on the iron geochemical characteristics of the analyzed lavas. These authors suggested that the oxygen fugacity at this volcanic arc is associated with primary slab/mantle melting processes rather than a crustal control. Moreover, the oxygen fugacity is proposed to be higher near the trench, decreasing towards the back arc (Grocke et al., 2016). As observed, the $^{238}\text{U}$ excess increases eastwards for the San Pedro-Linzor volcanic chain (Fig. 4b) which is opposite to the increasing oxygen fugacity trend proposed for the Central Andean volcanic arc (Grocke et al., 2016). Thus, variations in $^{238}\text{U}$ excess are not associated with mantle in-growth below the San Pedro-Linzor volcanic chain.

Within other magmatic systems in the Andes, $^{238}\text{U}$ depletion (i.e.
$^{230}$Th enrichment), and high LREE/HREE ratios have been related to garnet fractionation at lower levels in the thick crust (Garrison et al., 2006; Hora et al., 2009; Mamani et al., 2010). As the analyzed lavas show $^{238}$U enrichment (Fig. 4b), no involvement of garnet fractionation is suggested in the evolution of the San Pedro-Linzor volcanic chain, which has also been proposed for other products of the main arc at the Altiplano-Puna Volcanic Complex using LREE/HREE ratios (Godoy et al., 2019).

Given the lack of correlation between fluid mobile/immobile elements and $^{238}$U/$^{232}$Th, we suggest that the U-series disequilibria in the San Pedro-Linzor lavas is mostly controlled by processes associated with magmatic differentiation rather than by the source, which occurs...
mainly at upper-crustal levels (i.e. Shallow-MASH; Godoy et al., 2014, 2019; González-Maurel et al., 2020). Data falling near or on the equiline is associated with stagnation of magmas > 350 kyr (Bourdon et al., 2000; Kiebala, 2008) (Fig. 4a). The observed disequilibria (Figs. 4 and 5) for the volcanic chain suggest that these upper crustal magmatic processes occurred in the last 350 kyr, as indicated for other Andean volcanoes (e.g. Bourdon et al., 2000; Garrison et al., 2006; Kiebala, 2008). Thus, the main differentiation processes established for the volcanic chain (i.e. FC, AFC, and ATA; Fig. 2) are used here to constrain the evolution of U-series disequilibria in the last 350 kyr.

5.1.1. The role of amphibole fractionation

The different trends observed for \((238\text{U}/232\text{Th})\) with evolution of San Pedro Young and La Poroña (Fig. 4) suggests that \((238\text{U}/232\text{Th})\) variations are related to upper crustal differentiation processes in which a mineralogical phase fractionates when silica content increases over 62 wt%. Garrison et al. (2006) described the presence of allanite and apatite in rhyolitic lavas sampled from Cotopaxi (Northern Andes, Ecuador). These authors related the U-enrichment of these lavas to

\[\text{apatite in rhyolitic lavas sampled from Cotopaxi (Northern Andes, Ecuador)}\]

Garrison et al. (2006) described the presence of allanite and apatite in rhyolitic lavas sampled from Cotopaxi (Northern Andes, Ecuador). These authors related the U-enrichment of these lavas to amphibole crystallization, as this phase retains Th during differentiation processes in which a Th-retaining mineral is fractionated at depths < 25 km (Feeley and Davidson, 1994; Matthews et al., 1994; Burns et al., 2015; Gorini et al., 2018) and can be associated with the evolution of the Altiplano–Puna Magma Body (Burns et al., 2015; Gorini et al., 2018). This is also recognized at the San Pedro–Linzor volcanic chain, where amphibole is an important mineral phase mainly in lavas with SiO2 content > 62 wt% (O'Callaghan and Francis, 1986; Godoy et al., 2018; González-Maurel et al., 2019a). This phase (Fig. 3), is related to the decrease of CaO + Al2O3 (wt. %; Fig. 6c) and Dy/Dy* (after Davidson et al., 2013) with differentiation (Fig. 7a). Thus, the relationship between decreasing CaO + Al2O3 (wt. %) and Dy/Dy* with increasing \((238\text{U}/232\text{Th})\) (Figs. 6d and 7b) suggests that the \(238\text{U}\) excess can be related to amphibole crystallization, as this phase retains Th during differentiation (e.g. Berlo et al., 2004; Jicha et al., 2005; Garrison et al., 2006; Huang et al., 2008; Horá et al., 2009). Therefore, although partition coefficients for amphibole for U and Th are < 1, the bulk \(\text{D}_{\text{U/Th}}\) ratio for this mineral (< 1) and the importance of this mineralogical phase in the magmatic evolution of the Central Andes suggest that amphibole crystallization is responsible for the relatively high \((238\text{U}/232\text{Th})\) ratios recognized during evolution of San Pedro (Young and Old) and Paniri lavas.

\[\langle 230\text{Th}, 232\text{Th}\rangle_0\) ratios for San Pedro Young are substantially higher than for San Pedro Old (Fig. 7c), which is significant compared to the other analyzed volcanic suites with old and young phases (Figs. 3d and 7c). \(230\text{Th}\) in-growth by radioactive decay of \(238\text{U}\) has been related to an increase of \((230\text{Th}/232\text{Th})_0\) in magmas during stagnation in shallow chambers (Condones et al., 2003; Peate and Hawkesworth, 2005). Thus, we propose that the negative correlation of \((230\text{Th}/232\text{Th})_0\) with Dy/Dy* (Fig. 7c) for lavas of San Pedro Young is indicative of \(230\text{Th}\) in-growth during FC differentiation from olivine-pyroxene-bearing to

\[\text{apatite in the control of the observed 238U enrichment of the analyzed samples.}\]

Garrison et al. (2006) suggested that \(238\text{U}\) excess can be generated by assimilation of an amphibole-bearing crust. At the Altiplano–Puna Volcanic Complex, amphibole is an important mineralogical phase (i.e. O'Callaghan and Francis, 1986; Feeley and Davidson, 1994; Burns et al., 2015; Gorini et al., 2018), which fractionates at depths < 25 km (Feeley and Davidson, 1994; Matthews et al., 1994; Burns et al., 2015; Gorini et al., 2018) and can be associated with the evolution of the Altiplano–Puna Magma Body (Burns et al., 2015; Gorini et al., 2018). This is also recognized at the San Pedro–Linzor volcanic chain, where amphibole is an important mineral phase mainly in lavas with SiO2 content > 62 wt% (O'Callaghan and Francis, 1986; Godoy et al., 2018; González-Maurel et al., 2019a). This phase (Fig. 3), is related to the decrease of CaO + Al2O3 (wt. %; Fig. 6c) and Dy/Dy* (after Davidson et al., 2013) with differentiation (Fig. 7a). Thus, the relationship between decreasing CaO + Al2O3 (wt. %) and Dy/Dy* with increasing \((238\text{U}/232\text{Th})\) (Figs. 6d and 7b) suggests that the \(238\text{U}\) excess can be related to amphibole crystallization, as this phase retains Th during differentiation (e.g. Berlo et al., 2004; Jicha et al., 2005; Garrison et al., 2006; Huang et al., 2008; Horá et al., 2009). Therefore, although partition coefficients for amphibole for U and Th are < 1, the bulk \(\text{D}_{\text{U/Th}}\) ratio for this mineral (< 1) and the importance of this mineralogical phase in the magmatic evolution of the Central Andes suggest that amphibole crystallization is responsible for the relatively high \((238\text{U}/232\text{Th})\) ratios recognized during evolution of San Pedro (Young and Old) and Paniri lavas.

\[\langle 230\text{Th}, 232\text{Th}\rangle_0\) ratios for San Pedro Young are substantially higher than for San Pedro Old (Fig. 7c), which is significant compared to the other analyzed volcanic suites with old and young phases (Figs. 3d and 7c). \(230\text{Th}\) in-growth by radioactive decay of \(238\text{U}\) has been related to an increase of \((230\text{Th}/232\text{Th})_0\) in magmas during stagnation in shallow chambers (Condones et al., 2003; Peate and Hawkesworth, 2005). Thus, we propose that the negative correlation of \((230\text{Th}/232\text{Th})_0\) with Dy/Dy* (Fig. 7c) for lavas of San Pedro Young is indicative of \(230\text{Th}\) in-growth during FC differentiation from olivine-pyroxene-bearing to

\[\text{apatite in the control of the observed 238U enrichment of the analyzed samples.}\]
amphibole-bearing suites within shallow crustal magmatic chambers (González-Maurel et al., 2019a). This also is plausible for the more evolved lavas of Paniri volcano, although to a lesser extent (Fig. 7c).

5.1.2. The role of crustal contamination and mafic inputs

Except for San Pedro Young, all suites show a positive correlation between \( (230\text{Th}/232\text{Th})_0 \) and \( 87\text{Sr}/86\text{Sr} \) (Fig. 3d). This indicates that both ratios are mainly associated with crustal contamination (e.g. Huang et al., 2008), which is an important process at San Pedro-Linzor volcanic chain (Godoy et al., 2017, 2018; González-Maurel et al., 2019a,b, 2020), and the Central Andes (e.g. Davidson et al., 1990; Feeley et al., 1993; Matthews et al., 1994; Taussi et al., 2019). This contamination is related to differentiation processes occurring due to magma stagnation during which \( 230\text{Th} \) in-growth is generated (Fig. 7c). Thus, the most evolved, and least contaminated (Fig. 2a), products of La Poruña and San Pedro Old show low \( (230\text{Th}/232\text{Th})_0 \) (Fig. 4c). This highlights the ATA processes proposed for these volcanic structures, on which contamination (indicated by \( 87\text{Sr}/86\text{Sr} \) and \( 230\text{Th}/232\text{Th})_0 \)) decreases with the increasing silica content of the magmas (González-Maurel et al., 2019a,b). Jicha et al. (2005) proposed that abrupt shifts in magmatic evolution toward successively lower \( (230\text{Th}/232\text{Th})_0 \) reflect the influx of magma into the system or the mixing of newly arrived magma with melt that remained in the deep reservoir. Thus, the lowest \( (230\text{Th}/232\text{Th})_0 \) obtained for the youngest product of Paniri (Figs. 4d and 7c) indicates a magmatic recharge occurring in the related magmatic system, as these recharging magmas would have \( 87\text{Sr}/86\text{Sr} \) ratios < 0.706 in the Central Andes (Burns et al., 2015, 2020; Godoy et al., 2017; de Silva and Kay, 2018).

5.1.3. Upper crustal evolution and 238U-230Th systematics at San Pedro-Linzor volcanic chain

The obtained \( 238\text{U}/230\text{Th} \) data for the San Pedro-Linzor volcanic chain allows us to re-evaluate the existing ideas on magma genesis in the volcanic chain, and the Altiplano-Puna Volcanic Complex. Thus, we propose that the \( (238\text{U}/232\text{Th}) \) observed for analyzed products older than 100 ka (i.e. San Pedro Old and Paniri) are related to assimilation of an upper crustal source that mainly fractionated plagioclase + amphibole ± pyroxene, as indicated by Godoy et al. (2018) and González-Maurel et al. (2019a) (Fig. 8). For San Pedro Old, ATA differentiation generates an increase of amphibole fractionation with decreasing Sr-isotope content of the lavas (González-Maurel et al., 2019a), which leads to the negative correlation between \( (238\text{U}/232\text{Th}) \) with \( 87\text{Sr}/86\text{Sr} \) (Fig. 4c), and \( \text{Dy/Dy}^* \) (Fig. 7b). However, as no significant stagnation of magmas occurs, \( 230\text{Th} \) in-growth is not developed (Fig. 7c). Evolution of Paniri by AFC increases \( (238\text{U}/232\text{Th}) \), \( (230\text{Th}/232\text{Th})_0 \), and \( 87\text{Sr}/86\text{Sr} \) with differentiation (Fig. 4c-d), during which amphibole fractionation occurred. After this stage, a change in the dominant mineralogy of the system is proposed for the products that were erupted in the last 100 kyr (González-Maurel et al., 2019a) (Fig. 8). This change involves fractionation of plagioclase + olivine + pyroxene in the less evolved magmas (Godoy et al., 2018; González-Maurel et al., 2019a), which decreases the \( (230\text{Th}/232\text{Th}) \) of La Poruña, and the less-evolved products of San Pedro Young and Paniri (Figs. 3c and 7b). The decrease in \( (230\text{Th}/232\text{Th})_0 \) with \( 87\text{Sr}/86\text{Sr} \) in the youngest volcanic product of Paniri (Fig. 4d) suggest that the mineralogical change is due to new mafic injections from a deeper source (Fig. 8) (e.g. Burns et al., 2020), which also progressively lowers the initial \( 87\text{Sr}/86\text{Sr} \) and \( (230\text{Th}/232\text{Th})_0 \) of the
analyzed volcanic structures with time (González-Maurel et al., 2019a). The development of shallow (4–8 km depth) magmatic chambers below San Pedro volcano allows FC evolution during which amphibole crystallizes, which causes $^{238}\text{U}$ decay and $^{230}\text{Th}$ in-growth. We suggest that this new mafic input could trigger the eruption of the nearby Chao Dacite and Chillahuita domes (Figs. 1 and 8) of ca. 100 ka (Tierney et al., 2016), which are coeval with La Poruña, the first stages of San Pedro Young and the youngest event of Paniri. Mafic input as a possible eruption trigger is proposed for other enclave-hosting domes of the Central Andes (e.g. Watts et al., 1999; Taussi et al., 2019; Godoy et al., 2019; Burns et al., 2020).

6. Conclusions

To completely understand the U-series disequilibria signatures of a particular magmatic system it is important to establish its origin and evolution using a combination of detailed whole-rock geochemistry (e.g. major oxide, trace and rare earth elements, and Sr and Nd radiogenic isotopes), and geochronological and stratigraphic information. The U-series characteristics of the San Pedro-Linzor volcanic chain are mostly related to the upper crustal evolution of subduction-related mantle-derived magmas, previously defined using detailed geological, geochemical and radiogenic isotope characteristics. The U-series isotopic signature therefore recorded: i) the different degrees of interaction of mantle-derived magmas with partially molten upper crustal layers, ii) the differentiation processes during ascent to the surface, and iii) new mantle-derived mafic injections. This shows that $^{238}\text{U}$ and $^{230}\text{Th}$ changes in this volcanic chain in the Central Andes are related to magmatic evolution at upper crustal levels. U-series systematics in this, and similar complex tectonic environments, is therefore not necessarily dominated by fluid addition into the mantle wedge.

Author statement


Declaration of competing interest

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.

Acknowledgments

This work was funded by the Comisión Nacional de Investigación Científica y Tecnológica [FONDECYT Postdoctorado Nº 3160432 to B.G.; CONICYT-PCHA/Doctorado Nacional/2015–21150403 to O.G.-M.], and Centro de Excelencia en Geotermia de los Andes- Universidad de Chile [FONDAP-CONICYT 15090013]. We also thank Dr. Andrés...


