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### ► To cite this version:

Diego Narvaez, Estelle F. Rose-Koga, Pablo Samaniego, Kenneth T. Koga, Silvana Hidalgo. Constraining magma sources using primitive olivine-hosted melt inclusions from Puñalica and Sangay volcanoes (Ecuador). *Contributions to Mineralogy and Petrology*, 2018, 173 (80), 10.1007/s00410-018-1508-8. hal-01962618

**HAL Id: hal-01962618**

**<https://uca.hal.science/hal-01962618v1>**

Submitted on 26 Nov 2020

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1 **Constraining magma sources using primitive olivine-hosted**

2 **melt inclusions from Puñalica and Sangay volcanoes (Ecuador)**

3  
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5  
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11  
12 **Abstract**

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14  
15 **Key words:** Melt inclusions, olivine, primary magmas, volatile elements, subduction zone, Ecuador.

16

## 18 **Introduction**

19       Theoretical and experimental studies on dehydration and melting reactions which occur during subduction have  
20 identified two different slab components (e.g. [Elliott 2003](#); [Kessel et al. 2005](#); [Spandler and Pirard 2013](#)). On the one  
21 hand, the dehydration of the subducted slab produces a low-density aqueous phase (hereafter called “fluid”), which is  
22 characterized by enrichment in large-ion lithophile elements (LILE, e.g. B, Rb, Ba, Pb) coupled with low concentrations  
23 of high-field strength elements (HFSE, e.g. Nb, Ta, Zr) and heavy rare earth elements (HREE, e.g. Yb and Y). On the  
24 other hand, the partial melting of the subducted slab (i.e. the altered oceanic crust and/or the sedimentary cover)  
25 produces a high-density hydrous siliceous phase (hereafter called “melt”), which is enriched in the so-called fluid-  
26 immobile elements, such as the light rare earth elements (LREE, e.g. La, Ce), HFSE (e.g. Nb), as well as some LILE  
27 (e.g. Be, Th). These fluids and/or melts percolate into the hotter and shallower mantle wedge, decreasing its solidus  
28 temperature and triggering its partial melting via a porous flow process ([Grove et al. 2012](#)). Hence, the trace element  
29 signature of primitive arc magmas is typically ascribed to the nature of the subduction component (fluid or melt; e.g.  
30 [Elliott et al. 1997](#); [Class et al. 2000](#); [Labanieh et al. 2012](#)), whereas its major element composition is mainly controlled  
31 by the mineralogy of the mantle wedge (e.g. [Grove et al. 2002](#)).

32       The dichotomy between fluids and melts issued from the subducted slab was corroborated by numerical models of  
33 the thermal regime of subduction zones around the world (e.g. [Syracuse et al. 2010](#)). These models take into account the  
34 geodynamic parameters of subduction systems (age and geometry of the slab, convergence rate, etc.) as well as a  
35 temperature- and stress-dependent mantle rheology, yielding large temperature variations at the slab-mantle wedge  
36 interface. In some cases, such as Cascadia, Mexico, or the Andean Colombia-Ecuador subduction systems, the  
37 estimated temperatures are high enough to confirm the partial melting hypothesis of the subducted sediments and the  
38 altered oceanic crust ([Syracuse et al. 2010](#); [Gomez-Tuena et al. 2011](#); [Wallowski et al. 2015](#)). The Ecuadorian segment  
39 of the Andean Northern Volcanic Zone (NVZ) represents a unique place to test the influence of subduction parameters  
40 on the thermal regime and thus the slab component signature of primitive arc magmas. In fact, the Ecuadorian volcanic  
41 arc is characterized by an along-arc change in both the subduction parameters (age and geometry, [Yepes et al. 2016](#)),  
42 and the geochemical signature of the eruptive products ([Hidalgo et al. 2012](#); [Ancellin et al. 2017](#)), suggesting that the  
43 thermal regime is probably not the same along the length of the arc from north to south.

44       In this work, we identify the nature of the mantle source that melts to produce the primitive magmas of the  
45 Ecuadorian arc and the characteristics of the slab components added to this source. In order to fulfill these objectives,

46 we focused on the southern part of the Ecuadorian arc. This choice was based on two main reasons: first, this part of the  
47 Andean NVZ is developed above a young oceanic crust to the north, which is separated from an older oceanic crust  
48 located at the southern termination of the NVZ. Secondly, given that the differentiation processes (e.g. fractional  
49 crystallization, crustal assimilation, magma mixing, etc.) obscure the composition of the primitive magmas, the study of  
50 magma sources and slab components should be restricted to the most primitive lavas displaying a high Mg# (e.g.  
51 [Kelemen et al. 2014](#)). These kind of primitive magmas are common in the southern part of the Ecuadorian arc, namely  
52 at Puñalica and Sangay volcanoes. We sampled the most primitive rock of the whole Andean NVZ in this part of the  
53 arc, which is also one of the most primitive samples of the entire Andean arc (e.g. the SAN20B basalt from Sangay  
54 volcano, [Monzier et al. 1999](#)).

55 Several regionally oriented whole-rock geochemical studies have investigated the Ecuadorian arc magmatism  
56 ([Barragan et al. 1998](#); [Bourdon et al. 2003](#); [Garrison and Davidson 2003](#); [Bryant et al. 2006](#); [Chiaradia et al. 2009](#);  
57 [Samaniego et al. 2010](#); [Hidalgo et al. 2012](#); [Ancellin et al. 2017](#)). In this contribution, and following the melt inclusion  
58 (MI) work of [Le Voyer et al. \(2008\)](#) on volcanoes from the northern part of the Ecuadorian arc (Pichincha and Pan de  
59 Azúcar), we performed a similar approach by analyzing the major, trace element and volatile contents of a group of  
60 selected MIs trapped in the Mg-rich olivines hosted in primitive lavas from the southern part of the Ecuadorian arc  
61 (Puñalica and Sangay volcanoes). This work enabled us to constrain the mantle and slab components of the most  
62 primitive magmas studied in the NVZ and to relate them to the particular geodynamical setting of this part of the  
63 Andean arc. In addition, the new Sangay melt inclusion data represent a new example of primitive, Ca-rich, Ne-  
64 normative melt inclusions in a context of a volcanic arc constructed on a thick continental crust.

65

## 66 **Geodynamical and geological context**

### 67 1. Geodynamical setting of the Ecuadorian Andes

68 The Northern Volcanic Zone (NVZ) of the Andes stretches from ~6°N to ~2°S along the cordilleras of Colombia  
69 and Ecuador, and is situated at the convergent zone where the oceanic Nazca plate plunges under the continental South  
70 American plate (Fig. 1a). In Ecuador (i.e. from 1°N to 2°S), the relatively young Nazca plate (12-16 Ma; [Gutscher et al.](#)  
71 [1999](#); [Sallarès and Charvis 2003](#)) converges at an azimuth of N85°E, a rate of 5-6 cm/year ([Kellogg et al. 1995](#)) and a  
72 subduction angle of 25° ([Guillier et al. 2001](#)). In addition, at these latitudes the subducting Nazca plate hosts the  
73 Carnegie ridge, a 200-250 km-wide, 2 km-high submarine mountain range issued from the activity of the Galápagos  
74 hotspot. Based on geodynamic reconstruction, [Sallarès and Charvis \(2003\)](#) suggest that the portion of the Carnegie

75 ridge involved in the subduction system is younger than 10 Ma. Due to its morphology, the sedimentary blanket of the  
76 subducting Carnegie ridge is relatively thin (maximum 200-400 m, [Michaud et al. 2005](#); [Proust et al. 2016](#)). To the  
77 south (i.e. roughly to the south of 2-3°S), the subducting slab is older (25-30 Ma; [Gutscher et al. 1999](#)). The boundary  
78 between these two contrasting domains is the Grijalva Fracture Zone (GFZ), which consists of a 500 m-high escarpment  
79 separating a “young” crust which originated in the Galápagos spreading center to the north, and a relatively “old” crust  
80 formed at the East Pacific rise to the south. The inland prolongation of this structure was recently identified by [Yepes et](#)  
81 [al. \(2016\)](#) in the southern part of the Ecuadorian volcanic arc (Fig. 1b). These authors also show that the slab displays a  
82 bend around the GFZ that abruptly increases the angle of subduction from 20-25° to the north of the GFZ to 30-35°  
83 towards the south ([Yepes et al. 2016](#)).

84 The Ecuadorian segment of the NVZ is characterized by at least 84 volcanic centers of Pleistocene and Holocene  
85 age, which are distributed along four principal alignments constructed over different terranes of contrasting ages and  
86 lithologies ([Hall et al. 2008](#); [Hidalgo et al. 2012](#)). The crustal thickness is inferred to be >50 km beneath the active  
87 volcanic arc ([Feinenger and Seguin 1983](#); [Prevot et al. 1996](#); [Guillier et al. 2001](#)). Besides the primitive nature of the  
88 Puñalica and Sangay lavas, we chose these volcanoes for this study because they are *a priori* constructed on slab  
89 segments with different ages and seismic characteristics ([Yepes et al. 2016](#)). Puñalica is roughly above (or immediately  
90 to the north) of the GFZ projection, while Sangay lies to the south of this boundary. We expect that the presence of the  
91 GFZ in the Ecuadorian subduction system (i) might act as a preferred fluid transport region, and (ii) should allow us to  
92 identify different slab inputs from “young” and “old” slabs into the mantle wedge.

93

#### 94 Geological context of Sangay and Puñalica volcanoes

95 **Sangay** volcano (5230 m above sea level – a.s.l.) is the southernmost active edifice of the NVZ. It was constructed  
96 over the last 500 ka by three successive edifices ([Monzier et al. 1999](#)) separated by two major sector collapses whose  
97 deposits outcrop to the east, on the upper Amazonian plain. Sangay is thought to be located ~120-130 km (see red  
98 dotted line in Fig. 1b) above an old, seismogenic slab to the south of the GFZ ([Monzier et al. 1999](#); [Yepes et al. 2016](#))  
99 and is constructed on continental crust that consists of felsic and mafic igneous and metamorphic rocks ([Aspden and](#)  
100 [Litherland 1992](#); [Pratt et al. 2005](#)). In this work, we focus on the primitive basalt (SAN20B, Mg# 69, [Monzier et al.](#)  
101 [1999](#)), from the Sangay II edifice, roughly dated at between 100 and 50 ka. **Puñalica** volcano (3988 m a.s.l.) is a 300  
102 m-high, cone-shaped edifice slightly elongated in a north-south direction. It is constructed on the eastern flank of the  
103 Late Pleistocene Carihuairazo volcano ([Ordóñez 2012](#)). [Clapperton \(1990\)](#) and [Ordóñez \(2012\)](#) described a series of

104 lava flows from Puñalica that overly a sequence of tephra fallout deposits from the neighboring Chimborazo volcano  
105 ([Samaniego et al. 2012](#)). Based on this stratigraphic information, we expect an age younger than 18-25 ka for this  
106 edifice. The depth of the subducted slab at this location is ~120 km with the inland projection of the GFZ roughly below  
107 Puñalica volcano ([Yepes et al. 2016](#)). As for Sangay, we selected the most primitive lavas and tephras from Puñalica,  
108 which correspond to scoriaceous bombs sampled on the Puñalica cone (CAR83A, CAR96A and CAR113B), and a lava  
109 flow (RIO17A) that outcrops 4 km away from Puñalica's crater.

110

## 111 **Methodology**

### 112 Sample selection, olivine preparation and heating experiments

113 The chosen rocks (CAR83A, CAR96A, CAR113B, RIO17A from Puñalica, and SAN20B from Sangay volcano)  
114 were crushed and the 0.4-1.5 mm fraction was separated. We picked about 500 olivine crystals under a binocular  
115 microscope. We used crystal-bound to attach crystals onto glass slides in order to polish and select olivines in which  
116 melt inclusions were observed (about 100 crystals). We then selected about 50 crystals with melt inclusions bigger than  
117 30  $\mu\text{m}$ . All melt inclusions were crystallized and presented bubbles. Thus, we performed homogenization using a  
118 Vernadsky-type microscope heating stage following the method described by [Le Voyer et al. \(2010\)](#). A detailed  
119 description of melt inclusion homogenization procedure and analytical methods is provided in Online Supplementary  
120 Material 1. The data obtained for major elements by electron microprobe (EMP), volatile element concentrations by  
121 SIMS and trace element analysis by LA-ICPMS are provided in Table 1. We have taken specific care over the volatile  
122 element analysis in the MI (e.g. fluorine, chlorine) and post-analysis verifications of their quality such as the  
123 identification of misplaced beam-craters.

124

### 125 Post-entrapment crystallization correction

126 The composition of a melt inclusion can be modified by crystallization of olivine from the wall of the melt  
127 inclusion after its formation, by crystallization of minerals inside the melt inclusions during slow cooling or by over-  
128 dissolution of the olivine wall during heating stages. In order to account for these effects, after homogenization of the  
129 melt inclusions, the major element compositions of the melt inclusions were corrected numerically by dissolving/adding  
130 equilibrium olivine through iterative steps, recalculating the melt composition at every step until the melt reached Fe-  
131 Mg exchange equilibrium with the host olivine ([Le Voyer et al. 2008](#)). We used a  $K_d^{\text{Fe-Mg}}$  model to calculate the olivine

132 composition added to the MI (Toplis 2005). For the model calculation, we adopted the average homogenization  
133 temperature ( $1218 \pm 15^\circ\text{C}$ , min-max temperature range of  $1143\text{-}1309^\circ\text{C}$ ) and an oxidation state calculated following  
134 Wallace and Carmichael (1992). The speciation of sulfur was measured using the  $\text{S}^{2-}$  and  $\text{S}^{6+}$  peak positions in the melt  
135 inclusions obtained by the electron microprobe (Jugo et al. 2005). The  $\text{Fe}^{+3}/\Sigma\text{Fe}$  ratios for Puñalica melt inclusions vary  
136 from 0.16 to 0.23, while for Sangay the ratio is 0.28 for all melt inclusions (Table A1, Online Supplementary Material  
137 1). The resulting post-entrapment olivine crystallization correction for most melt inclusions was less than 10%, except  
138 for "BC" and "K" melt inclusions that reach 17 and 22 % respectively. In spite of the large corrections for these two  
139 MIs, we kept them in our database because their compositions are coherent with the others and thus they do not change  
140 our conclusions.

141

## 142 **Results**

### 143 Whole-rock petrological background of Sangay and Puñalica

144 *Sangay* samples display a high-K calc-alkaline magmatic series spanning from basaltic andesites to dacites (53.6-  
145 68.1 wt.%  $\text{SiO}_2$ , Fig. 2) and include a primitive basalt (SAN20B) that plots at lower silica content than the whole  
146 *Sangay* series (Fig. 2, 3). This latter is the most primitive basalt that has so far been sampled in the NVZ (Monzier et al.  
147 1999) with 50.3 wt.%  $\text{SiO}_2$ , 11.1 wt.%  $\text{MgO}$ , and a Mg# of 69 (Fig. 2, 3; Table 2). The high Ni, and Cr contents (273  
148 ppm Ni, 410 ppm Cr) and the relatively low  $\text{Al}_2\text{O}_3$  concentration (14.8 wt.%) corroborate its primitive character. The  
149 trace element abundances in SAN20B basalt show a typical arc pattern (e.g. enriched LREE and LILE, negative HFSE  
150 anomaly) and consistently plot at the primitive end of the *Sangay* series. It is worth noting that the Nb content in  
151 SAN20B basalt is slightly higher than that of the other NVZ basalts and basaltic andesites. Monzier et al. (1999)  
152 interpreted this feature as the result of partial melting of a relatively enriched mantle source. SAN20B mineralogy  
153 consists of phenocrysts of Mg-rich olivine (7 vol.%; up to 1 mm), and euhedral clinopyroxene (3 vol.%, 0.4-0.5 mm)  
154 surrounded by an intersertal groundmass consisting of clinopyroxene and plagioclase microlites. Olivine phenocrysts  
155 frequently include Cr-rich spinel inclusions. The Mg-rich olivines ( $\text{Fo}_{86-90}$ ) from this sample were selected for this  
156 study.

157 *Puñalica* lavas are medium-K calc-alkaline basaltic andesites and andesites (54.6-60.1 wt.%  $\text{SiO}_2$ , Fig. 2, 3; Table  
158 2), including some primitive andesites characterized by Mg# >60. On the basis of the MgO content, two groups are  
159 identified. A first group includes samples with low silica content (up to 57 wt.%  $\text{SiO}_2$ ) and variable MgO concentrations  
160 (4.3-7.8 wt.%), and a second group includes more differentiated magmas (58-60 wt.%  $\text{SiO}_2$ ) and homogeneous MgO

161 contents (4.8-6.2 wt.%). It is worth noting that the first group display large incompatible elements variations, namely  
162 for LREE (e.g. 15-35 ppm La) and LILE (4-9 ppm Th). The selected Puñalica samples correspond to both groups (Fig.  
163 2, 3; Table 2). They show variable phenocryst abundances of olivine (F<sub>080-86</sub>), orthopyroxene, clinopyroxene and  
164 plagioclase surrounded by an intersertal groundmass that includes plagioclase and clinopyroxene microlites. Olivine (up  
165 to 7 vol.%, up to 1 mm) forms euhedral and subhedral phenocrysts with homogeneous compositions.

166

167 Melt inclusion compositions

168 *Major elements*

169 Olivine-hosted (F<sub>086-89</sub>, Fig. 4a) melt inclusions from Sangay volcano are nepheline-normative (from 14.9 to 21.1,  
170 *Ne*, Table 1) and are characterized by restricted concentrations in SiO<sub>2</sub> (from 41.9 to 44.5 wt.%, expressed in a volatile-  
171 free basis, Fig. 3), MgO (6.4-9.1 wt.%) and FeOt (7.7-10.6 wt.%), as well as homogeneous Mg# values ranging from 59  
172 to 64 (Fig. 3, 4b). Sangay MIs mostly plot in the basaltic field belonging to a shoshonitic series (Fig. 2). In most Harker  
173 diagrams, Sangay MI compositions do not form an extension of the whole-rock trend (Fig. 3), showing higher contents  
174 in Al<sub>2</sub>O<sub>3</sub>, CaO and TiO<sub>2</sub> than their host lava. Sangay MI represent, together with Pan de Azúcar melt inclusions studied  
175 by [Le Voyer et al. \(2008\)](#), the most SiO<sub>2</sub>-poor magmas found in the Ecuadorian volcanic arc. Olivine-hosted (F<sub>082-86</sub>,  
176 Fig. 4a) melt inclusions from Puñalica display high-K calc-alkaline basaltic to basaltic andesitic compositions (Fig. 2),  
177 which are characterized by a variable content of SiO<sub>2</sub> (from 46.3 to 56.2 wt.%), MgO (3.9-10.2 wt.%) and FeOt (5.4-  
178 15.2 wt.%) (Fig. 3). The Mg# values vary from 53 to 58 (Fig. 4). As at Sangay, Puñalica MI have lower SiO<sub>2</sub> contents  
179 than Puñalica whole-rocks and do not form a continuous trend with them. Puñalica MI show higher contents of K<sub>2</sub>O,  
180 Na<sub>2</sub>O, FeOt and lower contents of TiO<sub>2</sub> and CaO than the values expected from the whole-rock trend at the same SiO<sub>2</sub>  
181 content (Fig. 2 and 3).

182

183 *Trace and volatile elements*

184 Sangay MI show trace element patterns typical of arc lavas and similar to those of Puñalica MI, except for the  
185 relatively high values of Ti and HFSE (e.g. Ta, Nb), expressed as a less marked negative anomaly in Nb (Fig. 5). The  
186 trace element patterns are also similar to those displayed by Sangay whole-rocks. Sangay MI have (La/Yb)<sub>N</sub> values  
187 ranging from 7 to 15 (normalized to primitive mantle, [Sun and McDonough 1989](#)). Puñalica MI are also enriched in  
188 LILE (e.g. Ba, K, Rb, Sr) and depleted in HREE (e.g. Yb) relative to MORB. The enrichment in LREE (e.g. La) relative



189 to HREE is represented as  $(La/Yb)_N$  and ranges from 5 to 45. These MI also display a marked negative anomaly in  
190 HFSE (e.g. Nb, Fig. 5). Three different MI groups are distinguished at Puñalica volcano based on trace and volatile  
191 elements concentrations (see below).

192 Sangay MI are volatile-rich, with H<sub>2</sub>O between 2.6 and 3.2 wt.% and CO<sub>2</sub> between 2776 and 6088 ppm. Puñalica  
193 melt inclusions vary from 0.05 wt.% to 3.1 wt.% H<sub>2</sub>O and from 29 to 4307 ppm CO<sub>2</sub> (Table 1). H<sub>2</sub>O concentrations  
194 measured in melt inclusions are considered as minimum values because melt inclusions are leaky containers for H<sub>2</sub>O  
195 (Chen et al. 2011; Gaetani et al. 2012). CO<sub>2</sub> concentrations are also considered minimum because melt inclusions could  
196 suffer from pre-entrapment CO<sub>2</sub> degassing due to degassing of CO<sub>2</sub> from the magma at depth.

197 Sangay MI are characterized by relatively high S concentrations (3836-5473 ppm), which overlap with the S  
198 concentrations of some Puñalica MI (most of them from CAR113B, Table 1). Melt inclusions from RIO17A have less  
199 S, between 2310 and 4335 ppm, with two inclusions more degassed in S at 906 and 1457 ppm. Samples from CAR83A  
200 have the least S (between 609 and 1571 ppm). The total range of S contents in melt inclusions from Sangay and Puñalica  
201 (609-5479 ppm) is similar to that of melt inclusions from other continental subduction zones such as Colima, Mexico  
202 (400-4900 ppm S; Vigouroux et al. 2008) and Mt. Shasta, California (in melt inclusions from High Alumina Olivine  
203 Tholeite, HAOT: 842-4800 ppm S; Le Voyer et al. 2010). Sangay MI are richer in F (627-1183 ppm) than melt  
204 inclusions from Puñalica (samples CAR96A, RIO17A and CAR83A, 439-1008 ppm, Table 1). Cl is the most contrasted  
205 volatile element. Sangay and Puñalica CAR83A melt inclusions have low and similar Cl concentrations (1636-2257  
206 ppm and 1352-1948 ppm, respectively), while all other Puñalica MI are Cl-rich, with concentrations between 4021-  
207 6112 ppm (Table 1). The Cl compositions of Sangay and most Puñalica MI are extremely high (maximum 6112 ppm  
208 Cl), only exceeded by rare melt inclusions (<9000 ppm) from Izu (Straub and Layne 2003), Aeolian (Métrich et al.  
209 1993, 2004; Vaggelli et al. 1993; Clocchiatti et al. 1994; Schiano et al. 2004; Spilliaert et al. 2006; Collins et al. 2009;  
210 Rose-Koga et al. 2012; Sorbadère et al. 2013) and Vanuatu arcs (Sorbadère et al. 2011; 2013). F concentrations are the  
211 highest found in arc melt inclusions to date. Overall, the halogen compositions (F and Cl) of the Sangay and Puñalica  
212 melt inclusions are high for continental arc settings, in the same range as that of the melt inclusions from the HAOT of  
213 Mt. Shasta, while Puñalica melt inclusions have the highest Cl concentrations so far reported for this type of  
214 geodynamic setting.

215

216 *Classification of Puñalica melt inclusion groups*

217 Based on the description of the chemical compositions of the Puñalica melt inclusions, we have defined three  
218 different groups. All these melt inclusions are trapped in Fo<sub>>82</sub> olivines and most of them have a lower SiO<sub>2</sub> content  
219 than the host lavas.

220 *Group 1* have the highest SiO<sub>2</sub> and the lowest MgO and FeO<sub>t</sub> contents and plot close to the trend drawn by the whole-  
221 rocks in Harker and trace element diagrams (Fig. 3 and 5). Group 1 consists of four MI found in sample CAR83A,  
222 which have similar trace element patterns to those of the whole-rocks, and the lowest LREE (e.g. La, Ce) values  
223 normalized to primitive mantle (Fig. 5). They are trapped in Fo<sub>83-84</sub> olivines. Their (La/Yb)<sub>N</sub> values vary from 5 to 14.  
224 Group 1 is also characterized by the lowest contents of Cl (1350-1950 ppm), F (439-560 ppm) and S (610-1570 ppm)  
225 compared to other groups of MI from Puñalica.

226 *Group 2* has similar compositions to Group 3 for FeO<sub>t</sub>, MgO and SiO<sub>2</sub>. Group 2 consists of twenty-six MI from  
227 CAR113B and RIO17A samples. Group 2 MI are enclosed in Fo<sub>84</sub> olivines. This group of MI show intermediate Cl  
228 (4037-6112 ppm) and F (483-1000 ppm) contents and (La/Yb)<sub>N</sub> values that vary from 9 to 25. A marked difference  
229 between CAR113B and RIO17A MI is the elevated S content, as CAR113B MI contains 1635 to 6738 ppm S and  
230 RIO17A from 906 to 4335 ppm S.

231 *Group 3* is depleted in Al<sub>2</sub>O<sub>3</sub> (Fig. 3) and enriched in trace elements compared to Groups 1 and 2. Group 3 consists of  
232 twelve MI from CAR96A. The olivine crystals are Fo<sub>83</sub>. Group 3 MI are characterized by high (La/Yb)<sub>N</sub> values that  
233 vary from 13 to 45, high Sc (up to 46 ppm, Groups 1 and 2 up to 23 ppm), high F (from 596 to 2187 ppm) and similar  
234 Cl (3460-5985 ppm) contents to those of Group 2. Moreover, Group 3 MI have LREE primitive mantle-normalized  
235 values (e.g. La, Ce), higher than the Puñalica whole-rocks (Fig. 5). Group 3 has the highest F concentrations (even  
236 compared to Sangay melt inclusions), all between 922 and 2187 ppm, except for one MI at 596 ppm (Table 1).

237

## 238 **Discussion**

239 Magmatic processes prior to entrapment

240 Melt inclusions may record dissolution-reaction-mixing (DRM) processes within the magmatic plumbing system  
241 (Danyushevsky 2004). These types of inclusions are commonly trapped in Fo<sub>>85</sub> olivines, and are numerous, often  
242 clustered in single crystals and are due to rapid crystallization. Such characteristics differ significantly from those of our  
243 samples. Puñalica and Sangay melt inclusions are trapped in primitive olivines, and the melt compositions are  
244 independent of the Fo content of the host crystal. Melt inclusions in our samples were scarce, and we never found

245 groups of melt inclusions in the same crystal as reported by [Danyushevsky \(2004\)](#). Based on these textural and  
246 compositional characteristics, the melt inclusions represent a primary inclusion character that formed at the time of the  
247 first growth of olivine. Thus, the compositions of the melt inclusions reported here have captured primitive melts that  
248 are different from host lavas. Our homogenization procedure and post-entrapment crystallization correction closely  
249 reconstitutes such primitive melt compositions at the time of capture, except for the abundance of H<sub>2</sub>O and CO<sub>2</sub> (which  
250 must be considered as minimum values).

251

252 Primitive magmas determined from melt inclusions

253 *Assessment of post-entrapment modifications*

254 Puñalica and Sangay melt inclusions are trapped in Fo<sub>82-86</sub> and Fo<sub>86-89</sub> olivines respectively. Compositional  
255 corrections for post-entrapment crystallization and degassing of melt inclusions are viable only for inclusions efficiently  
256 isolated from the influence of the external magma surrounding the host olivine. In fact, the composition of melt  
257 inclusions in readily exchanged major elements is susceptible to irreversible, post-entrapment modifications.  
258 Specifically, the host olivine can continuously exchange Fe and Mg with the surrounding magma, potentially leading to  
259 “Fe-loss” when comparing the melt inclusion composition to that of the whole-rock. Therefore, the exact reconstruction  
260 of the FeO and MgO contents of the parental magma cannot be achieved ([Danyushevsky et al. 2000](#); [Gaetani and](#)  
261 [Watson 2000](#); [Danyushevsky 2002](#)). However, most MI extend the whole-rock trend towards low silica compositions  
262 (excepting those from Puñalica Group 1 and Z, T and U from Group 2, Table 1), thus it seems reasonable to postulate  
263 that Fe-Mg exchange is limited. Other species, such as H<sup>+</sup> in melt inclusions, can also re-equilibrate with an external  
264 melt through the host olivine crystal and therefore the H<sub>2</sub>O contents of melt inclusions represent minimum H<sub>2</sub>O values  
265 and do not systematically represent either the initial H<sub>2</sub>O concentrations at the time of entrapment or the primitive H<sub>2</sub>O  
266 abundance ([Chen et al. 2011](#); [Gaetani et al. 2012, 2014](#)). Melt inclusions from this study are therefore considered as  
267 representative of minimum H<sub>2</sub>O concentrations of Puñalica and Sangay magmas and we will not use them in the rest of  
268 the discussion. Because trace elements (e.g. the rare earth elements) diffuse significantly more slowly than H<sup>+</sup>, Fe, and  
269 Mg ([Cherniak 2015](#)), abundances of such elements should closely resemble those at the time of entrapment following  
270 the crystallization correction (see section on post-entrapment crystallization correction in the supplementary material).  
271 Thus, the ratios of incompatible trace elements remain unmodified, as they are not partitioned into olivine, and are  
272 therefore representative of the primitive parental magma.

273

275 A petrogenetic decoupling between olivine-hosted melt inclusions and the host eruptive products (lavas and tephra)  
276 is clearly seen in Harker diagrams (Fig. 3). If the parental magma of the erupted products crystallized the olivines (with  
277 their inclusions), as it crossed the liquidus, the melt inclusion and lava/tephra compositions should plot along the  
278 olivine-controlled liquid line of descent (Fig. 3). We show the liquid line of descent calculated with R-MELTS  
279 algorithm (Gualda et al. 2015) from the more primitive MI compositions for both Puñalica (solid line) and Sangay  
280 (dashed line) magmatic suites, with a fixed pressure of 400 MPa, a  $fO_2$  at NNO and 4 wt.% H<sub>2</sub>O. The liquid-line-of-  
281 descent curves, for higher pressure values (i.e. 800 MPa, not shown), would display similar results. In fact, given that  
282 the first crystallization stages of Puñalica and Sangay MI are mainly controlled by olivine fractionation, there are almost  
283 no changes with pressure. Therefore, the Puñalica and Sangay host eruptive products cannot be derived from their  
284 respective melt inclusions by either simple olivine or olivine + clinopyroxene + plagioclase fractionation.

285 The projection from olivine into a Di-Ne-Q ternary plot (Fig. 6) yields additional constraints on the genesis of these  
286 MI. This projection from the olivine apex allows us to avoid any correction effect or chemical exchange between the  
287 melt inclusion and the host olivine (e.g. Sorbadère et al. 2013a, b). When plotted on the Di-Ne-Q plane, the studied  
288 Puñalica whole-rock samples are hypersthene-normative, whereas most of the 42 olivine-hosted (Fo<sub>82-86</sub>, Fig. 4a) melt  
289 inclusions from Puñalica volcano are nepheline normative (up to 10.1 Ne, Table 1); only six (AA, AC, AG1, K, S1 and  
290 BB) are hypersthene normative. Sangay whole-rock (SAN20B) and melt inclusions are all nepheline normative (Fig. 6).  
291 Magma compositions of low pressure crystallization sequences (especially at anhydrous conditions) cannot plot across  
292 the boundary separating nepheline and hypersthene normative magmas, which is defined by the Di-An join (Fig. 6).  
293 Typical mineral phases crystallizing from a basaltic magma (ol+cpx+plg) define a Fo-Di-An plane, which is projected  
294 on the Di-Ne-Q plane as a line joining Di-An, and magmas plotting to the left of the line can only evolve further to the  
295 left with crystallization, and vice-versa for the right. Occurrence of these Ca-rich, Ne-normative primitive melts in  
296 continental arcs, like at Sangay, are scarce and so far have only been reported at Mt. Shasta, Cascades (Le Voyer et al.  
297 2010), Vulcano, Italy (Gioncada et al., 1998; Rose-Koga et al. 2012), Ambrym and Gaua, Vanuatu (Sorbadère et al.  
298 2013a, b), Grenada and St Vincent, Lesser Antilles (Bouvier et al. 2010), Batan, Philippines (Métrich et al. 1999),  
299 Lombok, Indonesia (Elburg et al. 2007) and Pan de Azucar and Pichincha, Ecuador (Le Voyer et al. 2008).

300 An alternative process to evolve magmas from the nepheline to hypersthene normative fields is fractional  
301 crystallization of silica-undersaturated minerals. For instance, amphibole crystallization can significantly increase the  
302 silica content in the residual liquid, eventually causing it to cross the nepheline-hypersthene divide (e.g. Frezzotti 2001).

303 It is possible to examine whether or not such processes are responsible for deriving the erupted lavas from the melt  
304 inclusion compositions by investigating trace element abundances and their variations. Because amphibole  
305 preferentially incorporates Dy over Yb and La, the role of amphibole during differentiation is illustrated by a La/Yb  
306 increase and a decrease in Dy/Yb during differentiation (Davidson et al. 2007). The Dy/Yb (not shown) is highly  
307 variable in all MI and does not form a clear negative correlation with SiO<sub>2</sub>. In addition to REE systematics, other  
308 observations argue against a role of amphibole fractionation in these inclusions. Significant amphibole fractionation is  
309 not expected in a basalt or primitive andesite at high temperature (e.g. Krawczynski et al. 2012) such as that recorded in  
310 the inclusions ( $T_{\text{homogenization}}=1218\text{ }^{\circ}\text{C}$ ).

311 In conclusion, these observations indicate that the melts trapped in olivine crystals are not the parental magmas of  
312 the erupted lavas. Puñalica and Sangay melt inclusions represents primitive melts that are not related to host eruptive  
313 products, extending the magmatic series towards low silica contents.

314

315 Mantle sources for Puñalica and Sangay primitive magmas

316 Experimental studies have striven to characterize the different lithologies melting under arcs (see Fig. 6 caption for  
317 references). The experimentally-determined fields for magma compositions issued from melting of different mantle  
318 lithologies (peridotite, pyroxenite) are reported in Fig. 6 for pressures between 0.5 and 3.5 GPa (see figure caption for  
319 references). Puñalica melt inclusions plot in the field of peridotite melts (dotted field in Fig. 6) for different pressures.  
320 Group 1 and Group 2 MI have compositions similar to peridotite-melts coming from lower pressures (up to 2 GPa; Fig.  
321 6) than Group 3 (up to 3.5 GPa). Such a discrepancy is mainly due to lower Al<sub>2</sub>O<sub>3</sub> contents of Group 3 MI (Fig. 3c, Fig.  
322 7), which is in agreement with peridotite melting experiments (e.g. Walter 1998). These experiments have shown that  
323 garnet stability increases with pressure, reducing the Al<sub>2</sub>O<sub>3</sub> content in the partial melt. The stability of garnet in Group 3  
324 MI is also shown by an increase in La/Yb when Al<sub>2</sub>O<sub>3</sub> decreases, creating a negative correlation (Fig. 7). Therefore, the  
325 chemical differences recorded by the Ne-normative Puñalica MI could be explained by variable depths of partial  
326 melting and thus the mineralogy of the mantle, with garnet probably present in Group 3 MI and spinel/plagioclase for  
327 Group 1 and 2 sources, implying a deeper origin for Group 3 compared to Groups 1 and 2.

328 The Sangay MI plot in the field of amphibole-bearing clinopyroxenite-derived melts (Fig. 6) occurring at pressures  
329 lower than 1.5 GPa and temperatures between 1200-1300°C (Médard et al. 2006). The homogenization temperature of  
330 Sangay MI varies from 1189 to 1254°C and is therefore in good agreement with the temperatures stipulated for  
331 amphibole-bearing clinopyroxenite-derived melts. The high CaO, relatively high FeO<sub>t</sub>, low silica contents and high Sc

332 contents (from 26 to 43 ppm, Table 1) of Sangay MI, are also in agreement with compositions coming from the partial  
333 melting of an amphibole-bearing clinopyroxenite lithology. In fact [Sorbadère et al. \(2013\)](#) proposed that compositions  
334 similar to those of Sangay MI could be produced by mixing between partial melts of amphibole-bearing clinopyroxenite  
335 and peridotite. The compositions of the Sangay MI correspond to an end-member of the amphibole-bearing  
336 clinopyroxenite-derived melt. Similar Ca-rich, Ne-normative melt inclusions from Pan de Azúcar volcano, located in  
337 the back-arc of the Ecuadorian Arc, were also interpreted as the result of melting of pyroxenite-rich lithologies ([Le  
338 Voyer et al. 2008](#)).

339 The presence of clinopyroxenitic lithologies in arc sources has been widely discussed in the literature (e.g. [Schiano  
340 et al. 2000](#); [Médard et al. 2006](#); [Sorbadère et al. 2013a, b](#)). Clinopyroxenite is probably found in the lower crust since  
341 the differentiation process of primitive basalt produces ultramafic cumulates (i.e. clinopyroxenites), allowing the  
342 magma to evolve toward andesitic compositions (e.g. [Greene 2006](#); [Blatter et al. 2013](#); [Nandeckar et al. 2014](#)). These  
343 ultramafic cumulates react with new ascending hydrous magmas triggering amphibole crystallization at the expense of  
344 clinopyroxene ([Smith 2014](#)), producing the amphibole-bearing clinopyroxenites. Then, the amphibole-bearing  
345 clinopyroxenite is melted when a new hot primitive magma ( $T > 1100^{\circ}\text{C}$ ) ascends through the clinopyroxenite.  
346 Alternatively, the amphibole-bearing clinopyroxenite delaminates and sinks into the hotter mantle wedge ([Smith 2014](#);  
347 [Jagoutz and Kelemen 2015](#); [Schmidt and Jagoutz 2017](#)). The lower solidus temperature and higher melt productivity of  
348 pyroxenites ([Hirschmann and Stolper 1996](#)) would promote olivine growth and enable entrapment of amphibole-bearing  
349 clinopyroxenite-derived melts.

350

351 Constraining the slab components by trace element systematics

352 Previous experimental studies have demonstrated the variable mobility of LILE, HFSE, REE and other trace  
353 elements (e.g. Li, Be) during the dehydration (low temperature) or melting (high temperature) process of the basaltic  
354 oceanic crust and/or its sedimentary cap ([Kessel et al. 2005](#); [Klimm et al. 2008](#); [Hermann and Rubatto 2009](#)). These  
355 studies show that aqueous fluids resulting from dehydration processes are enriched in fluid-mobile elements (e.g. Ba,  
356 Rb, Cs, Pb) and strongly depleted in fluid-immobile elements (e.g. Be, Nb, La, Th). In contrast, hydrous siliceous melts,  
357 resulting from a melting process, are enriched in both fluid-mobile and fluid-immobile elements. Based on this  
358 dichotomy, fluid-mobile/fluid-immobile element ratios have been used to identify the nature of the slab components  
359 (e.g. [Elliott et al. 1997](#); [Elliott 2003](#)). Fig. 8a, b shows plots of Sr/Th and Ba/Th, respectively vs.  $(\text{La}/\text{Yb})_{\text{N}}$  of the melt  
360 inclusions. Because the mobile/immobile element ratio (e.g. Ba/Th, Sr/Th) of the pre-metasomatized mantle wedge (i.e.

361 MORB composition) is low, the addition of aqueous fluids from the slab increases this ratio. In contrast, mantle  
362 metasomatism by hydrous silicate melts does not change the ratio due to the fact that both groups of elements (fluid  
363 mobile and immobile) are transported by siliceous melts. The melt inclusions from Puñalica plot at relatively low Ba/Th  
364 values (60 to 190, average  $90 \pm 34$ ) compared to the range of world-wide primitive arc magmas (Fig. 8b, dotted area).  
365 There is no significant contrast in Sr/Th between Groups 1, 2 and 3 of Puñalica MI (Fig. 8a). However, the three  
366 Puñalica groups have distinct and relatively constant Ba/Th ratios within each group (Fig. 8b). The combination of the  
367 low Ba/Th and  $(La/Yb)_N$  (values ranging from 10 to 40) for Puñalica melt inclusions is characteristic of magma most  
368 likely derived from the partial melting of a source metasomatized by hydrous siliceous melts. The mean values of  
369 Group 3 MI compositions for Ba/La~15, Ba/Th~66 and Th/La~0.22 contrast with the ratios obtained for Sangay MI  
370 (Ba/La~29, Ba/Th~261 and Th/La~0.11), and are in agreement with those reported by [Brandt et al. \(2017a\)](#) for the  
371 northern segment of Payenia volcanic field located in the Andean Southern Volcanic Zone (Ba/La=16, Ba/Th=63,  
372 Th/La=0.25) whose source is also interpreted as having been enriched by siliceous melts.

373 On the other hand, Ba/Th values from Sangay melt inclusions are around three times higher than those of Puñalica  
374 (from 230 to 280, average  $261 \pm 17$ ) and Sr/Th ratio is also high with values between 444 to 594 (Fig. 8a; Puñalica  
375 between 103 and 209). Although not exceptionally high, the higher values for both Sr/Th and Ba/Th in Sangay melt  
376 inclusions suggests that aqueous fluids might have metasomatized the source of Sangay. This aqueous fluid would have  
377 been enriched in fluid mobile elements such as Ba, Sr, Pb. In a previous whole-rock study on Pichincha Volcanic  
378 Complex (north of the Ecuadorian arc) a threshold value of Ba/Th  $\sim 200$  was used to distinguish magmas  
379 metasomatized by aqueous fluids (Ba/Th > 200) from hydrous siliceous melts ([Samaniego et al. 2010](#)). Based on this  
380 threshold value, the Ba/Th ratios of Sangay melt inclusions can be taken as resulting from aqueous fluid metasomatism.

381 We would stress that in the whole-rock studies at the southern termination of the Ecuadorian arc, this  
382 discrimination is not evident (e.g. [Ancellin et al. 2017](#)), possibly because of the overprint by crustal contamination that  
383 has blurred the geochemical signal, whereas olivine-hosted melt inclusions are shielded from this contamination.

384

#### 385 Modelling the metasomatized mantle source

386 In order to test the hypothesis that two different subduction components are injected from the slab into the mantle  
387 wedge, we performed a three-step trace element modeling procedure. Firstly, we considered the melting or dehydration  
388 of the oceanic crust for Puñalica and Sangay, respectively. Secondly, given that the sources for Puñalica and Sangay MI  
389 are different, we mixed the slab component with a depleted peridotite for Puñalica and with an amphibole-bearing

390 clinopyroxenite composition for Sangay. Finally, we melted these enriched source lithologies using a batch melting  
391 equation (Shaw 1970).

392 1. For the basalt partial melting step, we used the high-temperature experimental  $K_d$  (1000°C) from Kessel et al. (2005)  
393 and the average composition of the Carnegie ridge basalts (Harpp et al. 2005). This step, with a melting degree set at  
394 5% leaves an eclogitic residue. The degree of melting is imposed by the strong negative-Nb anomaly in the Puñalica  
395 MI. Such an anomaly is a characteristic only attained with >1 vol.% of rutile in the residue and accordingly to Gaetani  
396 et al. (2008), the rutile vol.% in the residue peaks at roughly 4% of melting. Between 4 and 5% melting does not change  
397 our conclusion. For sediment melting, we used the bulk distribution coefficients given by Plank (2005), and an average  
398 composition of sediments from the Nazca plate (Plank and Langmuir 1998). We set the melting degree at a fairly low  
399 value (i.e. 8 %). The dehydration process was modeled with the same parameters as for the melting except for  $K_d$ ,  
400 which was that given by Kessel et al. (2005) at low temperature (800°C).

401 2. The trace element composition of the depleted peridotite is from Workman and Hart (2005), and that of the  
402 clinopyroxenite from Smith (2014). The mixing proportion between slab fluid or melt component and the depleted  
403 source varies from 10:90 to 15:85. When the slab component is a siliceous melt, the amount of sedimentary melt  
404 relative to basaltic melt varies in a proportion of 0 to 20%.

405 3. For Puñalica MI, the metasomatized mantle melt is 10%, leaving a residue of ol:opx:cpx in a proportion of 68:20:12  
406 and a variable amount of grt (1-8 vol.%). We used the  $K_d$ s given by Halliday et al. (2005) for basaltic melts. For  
407 Sangay, the minerals in the residue after 5% of melting are ol:cpx:hbl:sp in a proportion of 24:70:2:4. This mineral  
408 assemblage was computed by R-Melts software (Gualda et al. 2012) at 1 GPa and 1 wt.% H<sub>2</sub>O for an amphibole-  
409 bearing clinopyroxenite composition (from Médard et al. 2006).

410 Results are plotted in Fig. 9 as multi-element diagrams normalized to primitive mantle values (Sun and McDonough  
411 1989). The Puñalica modelled composition fits very well with natural MI compositions, supporting the hypothesis that  
412 the metasomatic agent beneath Puñalica is a silicate melt (Fig. 9a). For Sangay, the modeled composition shows a  
413 reasonable agreement, although some differences (e.g. Rb, Nb) are highly source-dependent and can be explained by  
414 the scarce trace element data for amp-bearing clinopyroxenite compositions in the literature (Fig. 9b). Lastly, given the  
415 primitive signature of SAN20B whole-rock, we also modelled its origin as a result of a hydrous fluid-metasomatized  
416 peridotite (Fig. 9c). The parameters for dehydration were similar to those of Sangay MI modelling and the source was  
417 that of a depleted mantle (Workman and Hart 2005). The mixing proportion between the slab component and the mantle



418 was fixed at 15:85 and the partial melting of the mantle at 7%. The relatively good fit indicates an aqueous fluid as the  
419 metasomatic agent responsible for the composition of the SAN20B olivine-hosted melt inclusions.

420

421 Constraints provided by the volatile element compositions on the nature of the slab flux in a continental subduction  
422 zone

423 Sangay and Puñalica MI have high concentrations of fluorine and chlorine (Fig. 10), which is typical of volcanic  
424 arcs from continental subduction (e.g. Izu, [Straub and Layne 2003](#); Mt. Shasta, Cascades, [Le Voyer et al. 2010](#);  
425 Vulcano, Italy and Iwate, Japan, [Rose-Koga et al. 2012, 2014](#)). Puñalica Group 3 melt inclusions display amongst the  
426 highest F contents in continental arc-related MI (up to 2187 ppm F). This high F content is accompanied by high Cl  
427 concentrations (Cl commonly between 5000 and 6000 ppm in Puñalica MI). For comparison, an olivine-hosted melt  
428 inclusion from Reventador volcano has 3149 ppm chlorine and 549 fluorine ([Samaniego et al. 2008](#)) and Tungurahua  
429 melt inclusions have less than 1081 ppm chlorine ([Myers et al. 2014](#)).

430 High halogen contents in primitive arc magmas (the case of Puñalica) can be achieved by two processes ([van den](#)  
431 [Bleeken and Koga 2015](#)): (i) the subducted crust melts (rather than simply dehydrating), or (ii) the subducted crust is  
432 enriched in halogens and eventually melts/dehydrates. Thus, one explanation is that Puñalica volcano is roughly located  
433 above the Grijalva fracture zone and the higher permeability in the fracture zone enhances interactions with seawater  
434 (compared to a normal oceanic crust), thus increasing its F and Cl contents. Furthermore and because the Puñalica slab  
435 component seems to be a siliceous melt, this altered oceanic crust eventually melts driving F and Cl contents even  
436 higher ([van den Bleeken and Koga 2015](#)). Both fluorine and chlorine are incompatible in the typical mineral phases of a  
437 garnet-bearing peridotite ([van den Bleeken and Koga 2015](#)), therefore, those elements would leave the mantle during  
438 partial melting. For an amphibole-bearing source lithology, as in the case of Sangay MI, fluorine compatibility must  
439 change because this element is compatible in amphibole, whereas chlorine is not. This preference of amphibole for  
440 fluorine would affect F/Cl ratios. Thus, Sangay F/Cl ratios (0.35-0.53) that are higher than those from Puñalica (0.11 to  
441 0.39) could be explained by the interaction of ascending mantle-derived magma with an amphibole-bearing  
442 clinopyroxenite, likely enriched in F compared to Cl.

443

444 Slab components in the geodynamic context of the continental Ecuadorian arc and beyond

445 The origin of the metasomatic agent in the Ecuadorian arc has long been debated in the scientific literature.  
446 Some researchers consider that the metasomatic agent of the subarc mantle wedge is an aqueous fluid issued from

447 dehydration reactions of the slab (Barragan et al. 1998; Garrison and Davidson 2003; Bryant et al. 2006; Chiaradia et al.  
448 2009). Based on the overall adakitic signature of the Ecuadorian arc, other researchers consider that the metasomatic  
449 agent is a siliceous-melt associated with slab partial melting (Bourdon et al. 2003; Hidalgo et al. 2012). In addition,  
450 some long-lived volcanic complexes of the Ecuadorian arc are characterized by a progressive variation of the trace  
451 element signature that has been interpreted as a change of the metasomatic agent throughout its evolution. This  
452 variation in whole-rock trace elements, described at Cayambe (Samaniego et al. 2002, 2005); Illinizas (Hidalgo et al.  
453 2007), Mojanda-Fuya Fuya (Robin et al. 2009) and Pichincha (Samaniego et al. 2010), implies that the older magmas of  
454 these volcanic complexes came from a hydrous-fluid metasomatized mantle wedge, whereas the younger magmas are  
455 related to partial melting of a siliceous-melt metasomatized mantle wedge. Such a temporal evolution suggests a change  
456 from dehydration to partial melting of the slab that could be associated with an increase in the thermal regime along the  
457 slab due to the presence of the subducted Carnegie ridge (e.g. Yepes et al. 2016). In this context, the younger age and  
458 structure of the Carnegie ridge would induce an enhanced thermal gradient along the slab, which may trigger slab  
459 partial melting. This hypothesis is supported by thermal modeling studies (e.g. Syracuse et al. 2010) that estimate  
460 elevated slab-surface temperatures below the Ecuadorian arc.

461 In this work, we demonstrated that the subarc mantle below two of the southern Ecuadorian volcanoes is  
462 metasomatized by different slab components. The cause of such variation might be related to the geodynamical setting,  
463 where the Grijalva Fracture Zone (GFZ) sharply separates a young slab to the north from an older slab to the south. As  
464 recently pointed out by Yepes et al. (2016), this difference in age is coupled to a contrasted seismic behavior and an  
465 increase in the subduction angle: to the north of the GFZ, the slab displays low intermediary seismicity (50-150 km  
466 depth) and subducts at an angle of 20-25°, whereas to the south, the slab is highly seismogenic and plunges at a higher  
467 angle (30-35°). This contrasted seismic behavior could be associated with a different thermal regime on both sides of  
468 the GFZ (Yepes et al. 2016), which in turn could control the dehydration, and the melting process happening at depth.

469 Based on whole-rock major, trace element, and Sr-Nd-Pb isotopic signature of the Ecuadorian arc lavas, Ancellin et  
470 al. (2017) describe a N-S variation of the metasomatic agent along the entire Ecuadorian volcanic arc. They interpreted  
471 these along-arc variations as an increase of the slab input northward and southward on both sides of a divide that they  
472 placed at 0.5°S (i.e. at the latitude of the Carnegie ridge subduction). They concluded that the most likely process able to  
473 explain these variations is a variable influx of slab-derived fluids or melts. In the present olivine-hosted melt inclusion  
474 study, we refine the previous findings and argue that Puñalica MI come from a mantle wedge metasomatized by a  
475 hydrous siliceous melt, whereas Sangay MI are most likely produced by partial melting of a hydrous fluid  
476 metasomatized amphibole-bearing clinopyroxenite source.

477 In a more general context, the singularity of Sangay melt inclusions is striking in Fig. 6 and 9. High-Ca, Ne-  
478 normative primitive arc melts exist in other arc systems around the world (*cf.* the section on Primitive magmas  
479 determined from melt inclusions), but are not that common in continental subduction zone settings. However, whereas  
480 the crustal thickness in the previously mentioned arc systems (Cascades, Italy, Vanuatu) is around 20-30 km thick, the  
481 Ecuadorian continental arc is characterized by a very thick arc crust (> 50 km). The influence of crustal thickness on  
482 melt compositions is not new and has already been proposed for arc lavas (e.g. Wallace and Carmichael 1992). In the  
483 case of Sangay MI, we therefore have to reconcile the amphibole-bearing clinopyroxenite source (Ca-rich, Ne-  
484 normative melts), the high volatile (F and Cl) contents of MI and the high Fo of the host olivines, with the presence of a  
485 50 km-thick crust. One hypothesis is that melting of the amphibole-bearing clinopyroxenite happens at depth, probably  
486 at the interface between the lower crust and the upper mantle. In order to accommodate the deep origin of the MI and  
487 the required fast migration to the surface, the occurrence of trans-crustal major faults seems an important requirement.

488

## 489 **Conclusions**

490 Melts inclusions from Puñalica and Sangay volcanoes are Ca-rich and have mostly Ne-normative compositions.  
491 The magmas sampled as melt inclusions are not the parental magmas of the whole-rocks but they constitute exceptional  
492 compositions that show the complexity of the processes occurring at subduction zones and the heterogeneity of the  
493 sources of primitive arc magmas.

494 All melt inclusions from Puñalica have major element compositions similar to experimental melts derived from  
495 peridotite. Sangay MI have homogeneous compositions and their origin is attributed to mixing processes between melts  
496 derived from peridotite (represented by the whole-rock SAN20B composition) and amphibole clinopyroxene-rich  
497 sources.

498 The slab component that metasomatizes the mantle source of Puñalica volcano is a siliceous melt (low  
499 mobile/immobile ratios), which displays a variable enrichment in LREE. Moreover, the high content of volatiles (e.g. F,  
500 Cl) is attributed to the presence of the Grijalva Fracture Zone that separates a younger and hotter oceanic crust to the  
501 north from a colder and older oceanic crust to the south. Under Sangay volcano, the melt inclusions are produced by  
502 partial melting of metasomatized (most likely by aqueous fluids) amphibole-bearing clinopyroxenite source and the  
503 relatively higher F compared to Cl is likely due to fluorine enrichment in the source linked to fluorine compatibility  
504 with amphibole.

505 Ca-rich, Ne-normative primitive melts are scarce in subduction zone settings, specially those associated with thick  
506 continental crust, and could possibly be related to the presence of major trans-crustal faults.

507

508

## 509 **Acknowledgments**

510 This research was conducted as part of Diego Narvaez's PhD, which is financed by the Secretaría Nacional de  
511 Educación Superior, Ciencia, Tecnología e Innovación of Ecuador (SENESCYT, Ecuador) and the ARTS program of  
512 the French Institut de Recherche pour le Développement (IRD). It is part of a cooperation program carried out between  
513 the Instituto Geofísico, Escuela Politécnica Nacional (IGEPN), Quito, Ecuador and the IRD, through the Laboratoire  
514 Mixte International "Séismes et Volcans dans les Andes du Nord". ER-K acknowledges funding from the French INSU  
515 scientific program SYSTER. Thank you F. Van Wyk de Vries for This work also benefited from financial support from  
516 the Laboratory of Excellence ClerVolc. This is Laboratory of Excellence ClerVolc contribution n° XXXX.

517

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767

768 **Figure captions**

769 **Fig. 1 a** Geodynamical setting of Ecuadorian arc. **b** Schematic map of the main geological zones in Ecuador [modified  
770 from [Jaillard et al. \(2008\)](#)]. Analyses of melt inclusions were performed in rock samples from Sangay and Puñalica  
771 volcanoes (in red). Puñalica volcano is a small, young edifice associated with the older Carihuairazo volcano .  
772 Pichincha Volcanic Complex (Pichincha) and Pan de Azúcar volcanoes, which are mentioned in the text, are in cyan.  
773 White dashed line is the surface projection of the Grijalva fracture zone (GFZ) that affects subduction and separates old  
774 oceanic lithosphere to the south from young oceanic lithosphere to the north. This projection is based on the recent  
775 seismological work of [Yepes et al. \(2016\)](#) studying the flexure of the subducted slab along the GFZ

776

777 **Fig. 2 a** K<sub>2</sub>O vs. SiO<sub>2</sub> classification diagram ([Peccerillo and Taylor 1976](#)) of melt inclusions (homogenization-  
778 corrected compositions; colored diamonds and triangles) and whole-rocks (shaded areas and star symbols colored to the  
779 same as their corresponding MI) of Sangay and Puñalica volcanoes. 50 melt inclusion compositions are plotted; 7  
780 belonging to SAN20B sample from Sangay volcano and the others belonging to Puñalica samples. Groups 1, 2 and 3 in  
781 the legend box correspond to the groups defined for Puñalica MI. See text for more details. **b** Molar 100 \* (MgO /  
782 (FeO + MgO) vs. SiO<sub>2</sub> wt.% for melt inclusions and whole-rock lavas from Sangay and Puñalica volcanoes

783

784 **Fig. 3** Harker diagram showing the composition of MgO, FeO, Al<sub>2</sub>O<sub>3</sub> and CaO vs. SiO<sub>2</sub> for melt inclusions (  
785 homogenization-corrected compositions) and whole-rock samples (shaded areas) of Sangay and Puñalica volcanoes.  
786 The black arrows correspond to olivine fractionation lines calculated using R-MELTS program ([Gualda et al. 2015](#)),  
787 starting from one of the most primitive melt inclusions of each volcano, using a pressure of 4 kbar and an estimated  
788 water content of 2 wt. %. For description of symbols see Fig. 2

789

790 **Fig. 4** Frequency histogram of the forsterite content of the olivine phenocrysts (**a**) and of melt inclusions (**b**) from  
791 Puñalica and Sangay volcanoes. Diagram (a) shows data from this study and that of [Monzier et al. \(1999\)](#). Forsterite  
792 contents for melt inclusions are plotted using homogenization-corrected values and  $Fe^{2+}/\sum Fe$  obtained using sulfur  
793 speciation. We did not differentiate the Puñalica groups

794

795 **Fig. 5** Trace element compositions of Puñalica (**a-c**) and Sangay (**e**) melt inclusions and whole-rock lavas [shaded areas,  
796 [Hidalgo et al. \(2012\)](#) and [Ancellin et al. \(2017\)](#)] normalized to Primitive Mantle composition ([Sun and McDonough](#)

797 [1989](#)). **d** REE spider diagram for Puñalica MI. N-MORB (dashed gray line) from [Sun and McDonough \(1989\)](#) and E-  
798 MORB (dashed black line) from [Hofmann \(1988\)](#)

799

800 **Fig. 6** Projection from olivine (M<sub>2</sub>S) onto the Ne-Di-Qz (CMS<sub>2</sub>-S-CA) plane for whole-rock lavas and melt inclusions  
801 from Puñalica and Sangay. Schema using [O'Hara \(1976\)](#) CMAS component calculation. C = CaO – 10/3P<sub>2</sub>O<sub>5</sub> + 2Na<sub>2</sub>O  
802 + 2K<sub>2</sub>O, M = MgO + FeO + MnO – TiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub> + Na<sub>2</sub>O + K<sub>2</sub>O, S = SiO<sub>2</sub> – 2Na<sub>2</sub>O – 2K<sub>2</sub>O. Also  
803 shown in the diagram are the fields compiled by [Sorbadere et al. \(2013a\)](#) of experimentally determined melts of  
804 anhydrous ([Hirose and Kushiro 1993](#); [Baker and Stolper 1994](#); [Kushiro 1996](#); [Falloon et al. 2001](#); [Wasylenki et al.](#)  
805 [2003](#); [Laporte et al. 2004](#)) and hydrous peridotites between 0.5 and 3.5 GPa (continuous lines are isobars with pressure  
806 given in GPa; [Hirose and Kawamoto 1995](#); [Gaetani and Grove 1998](#)), amphibole-free ([Kogiso and Hirschmann, 2001](#))  
807 and amphibole-bearing clinopyroxenites between 0.5 and 1.5 GPa ([Médard et al. 2006](#); [Pilet et al. 2008](#))

808

809 **Fig. 7** La/Yb vs. wt.% Al<sub>2</sub>O<sub>3</sub> of melt inclusions and whole-rocks. La/Yb ratio is explained by 1 to 8% of garnet in the  
810 mantle residue following the model proposed for Puñalica MIs (see text)

811

812 **Fig. 8** Plot of (La/Yb)<sub>N</sub> normalized to primitive mantle ([Sun and McDonough 1989](#)) versus **a** Sr/Th and **b** Ba/Th.  
813 Whole-rock data variation for Pichincha Volcanic Complex field is taken from [Samaniego et al. \(2010\)](#). Purple field  
814 corresponds to the older Rucu Pichincha magmatic suite whereas yellow field corresponds to the field of the younger  
815 Guagua Pichincha suite. MORB composition represented by the small black rectangle is from [Leroux et al. \(2006\)](#). The  
816 primitive arc magma composition (dotted field) is taken from [Elliott \(2003\)](#). Symbols are those of Fig. 2

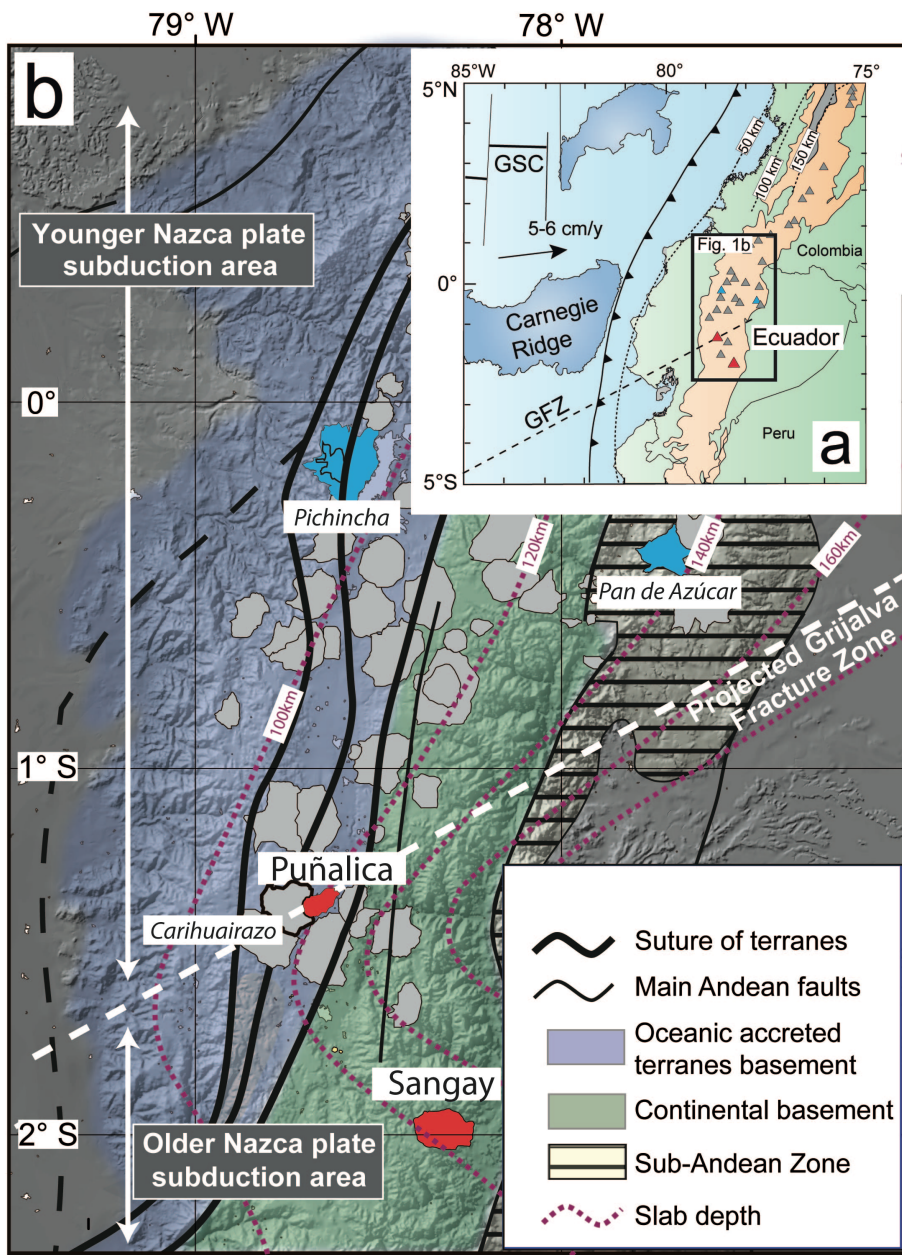
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818 **Fig. 9** Modeled composition (colored dashed lines) compared to natural melt inclusion (colored solid lines) from **(a)**  
819 Puñalica and **(b)** Sangay volcanoes. **(c)** Modeled composition for SAN20B whole-rock sample from Sangay volcano.  
820 Gray dot-dash lines are compositions of the non-metasomatized source lithologies: a depleted mantle ([Workman and](#)  
821 [Hart, 2005](#)) for Puñalica and SAN20B, and a clinopyroxenite ([Smith 2014](#)) for Sangay. The proportion of slab  
822 component compared to peridotite/clinopyroxenite in the mixing process is 10:90 for Puñalica MI, 12:88 for Sangay MI  
823 and 15:85 for SAN20B. The amount of sedimentary-origin melt in the slab component is 20% (only for Puñalica).

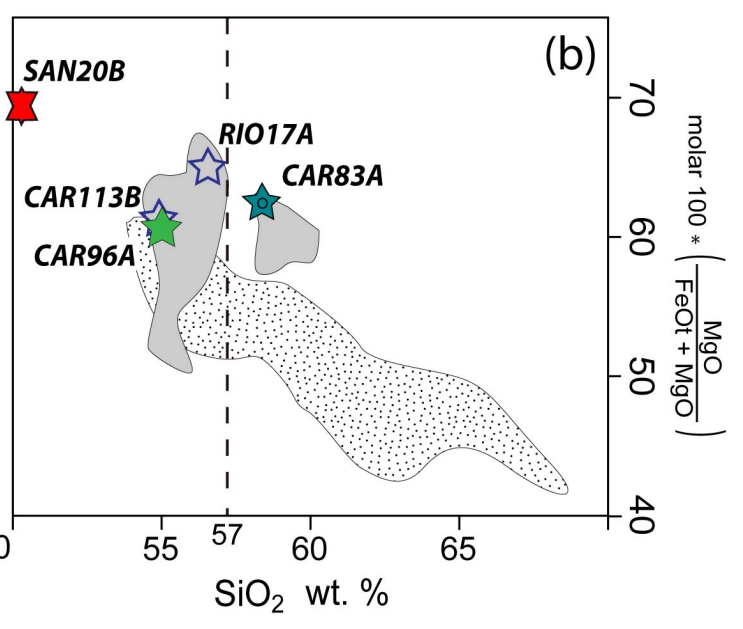
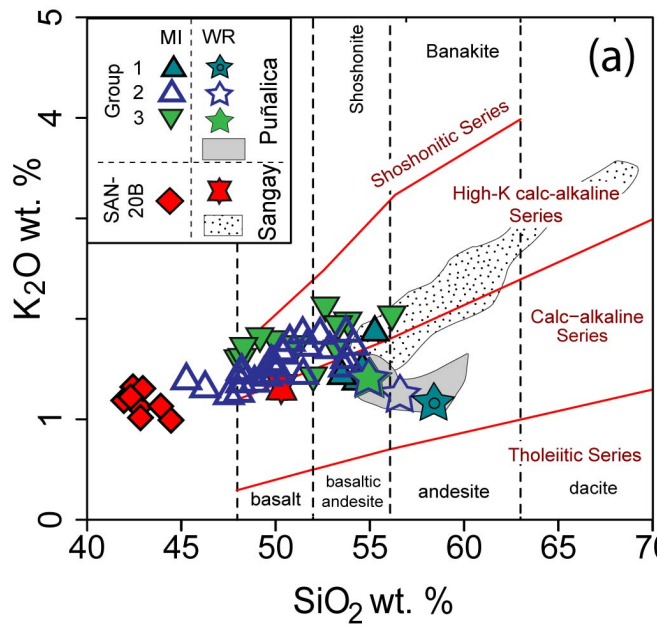
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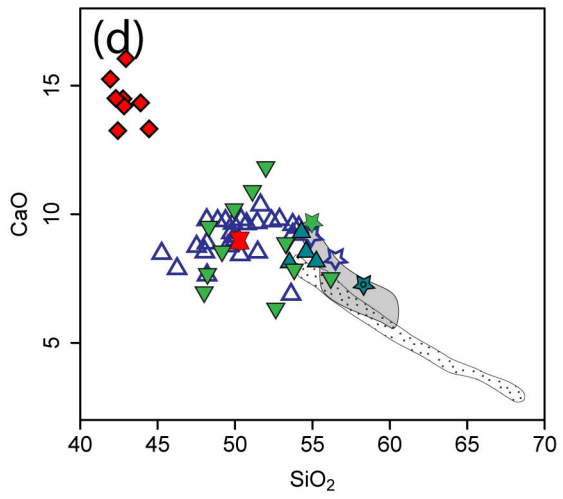
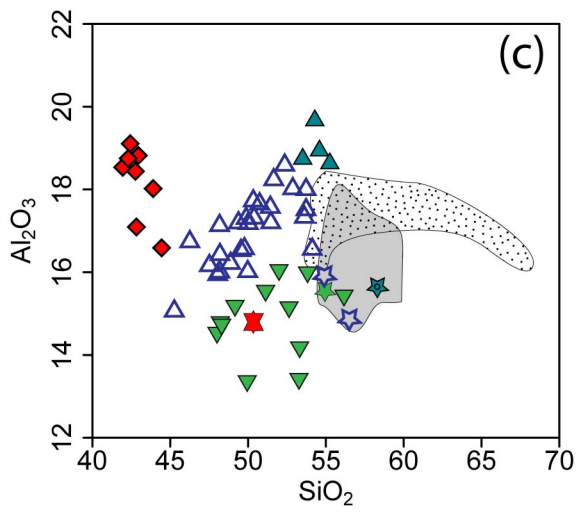
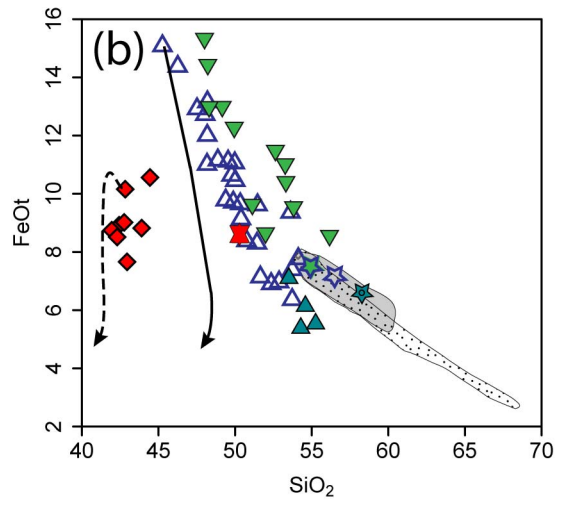
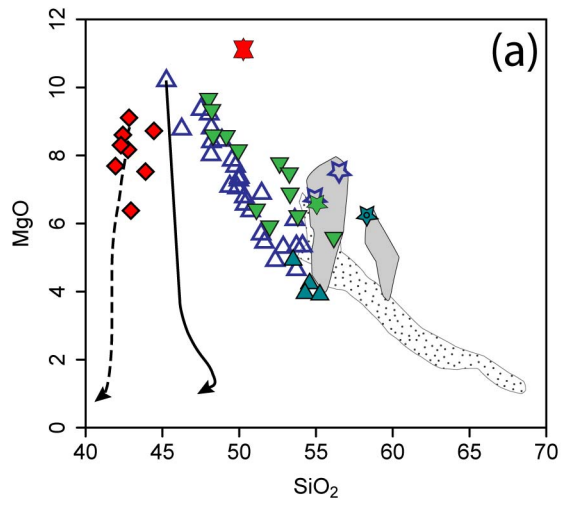
825 **Fig. 10** F vs. Cl for Sangay and Puñalica melt inclusions. Our data is compared to other melt inclusion compositions  
826 compiled by [Rose-Koga et al. \(2014\)](#). Melt inclusion compositions from Payenia backarc are from [Brandt et al. \(2017b\)](#).

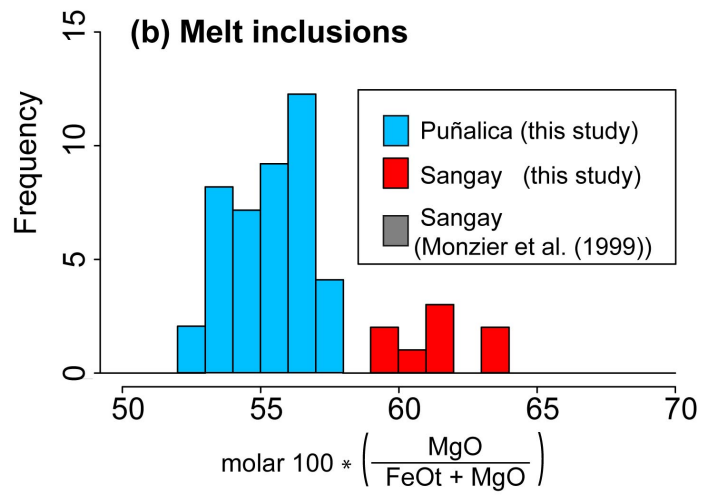
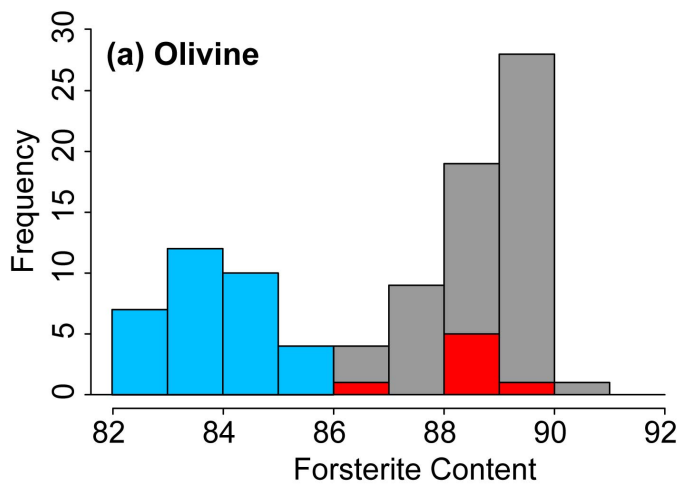
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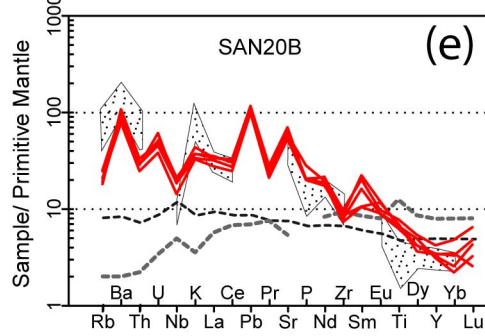
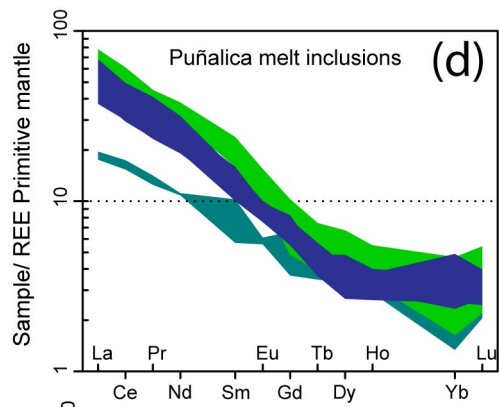
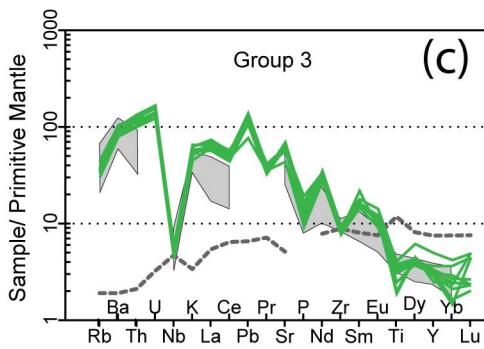
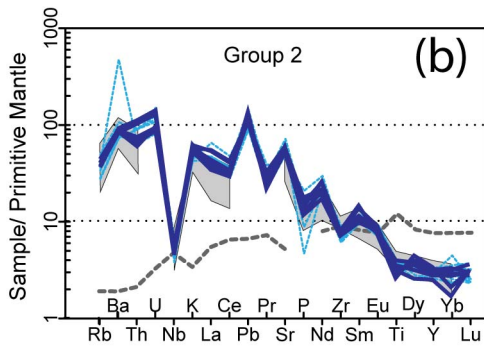
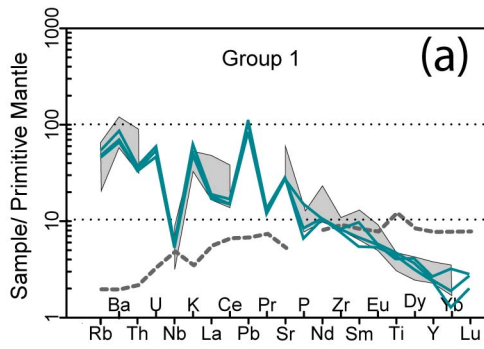




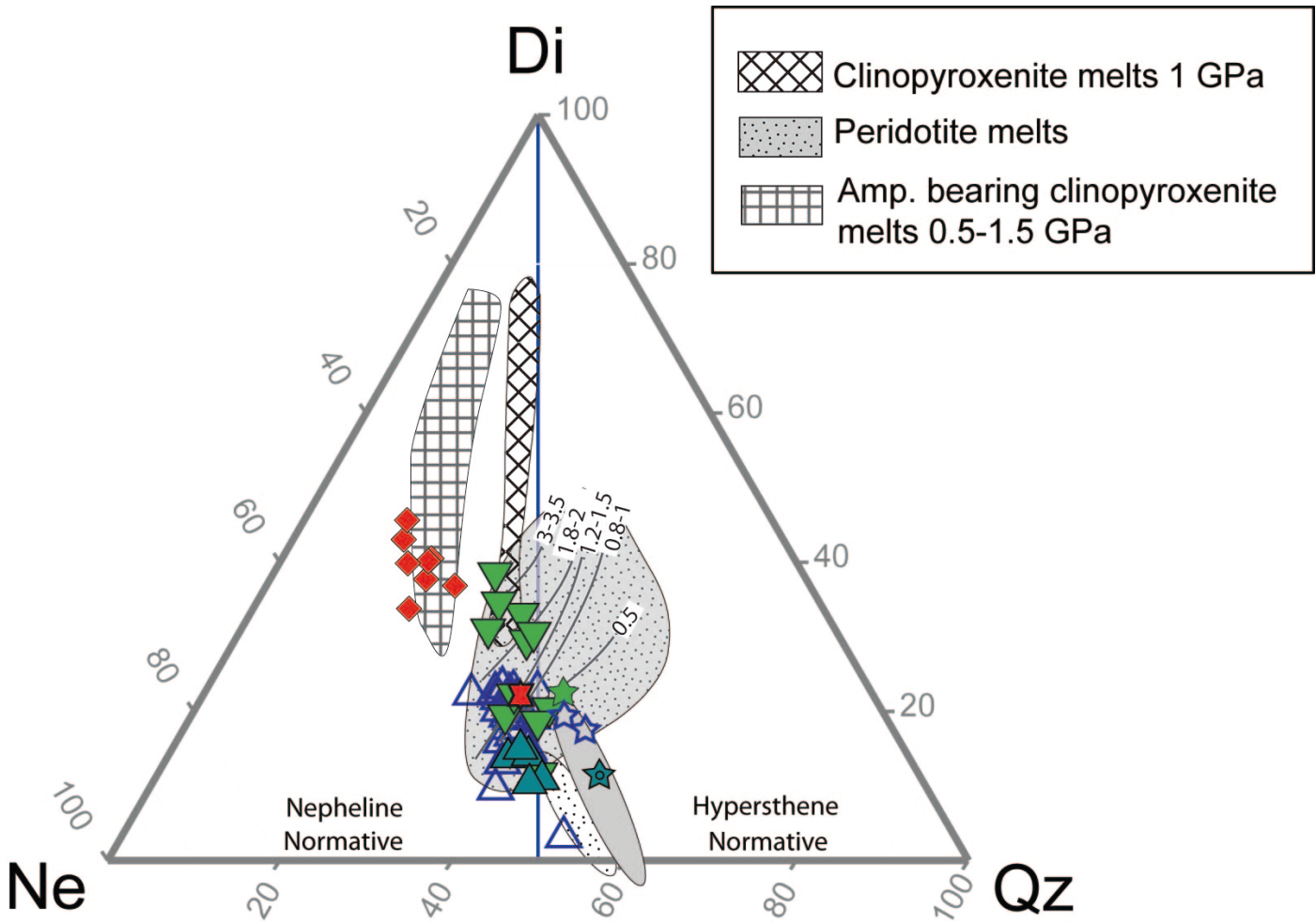


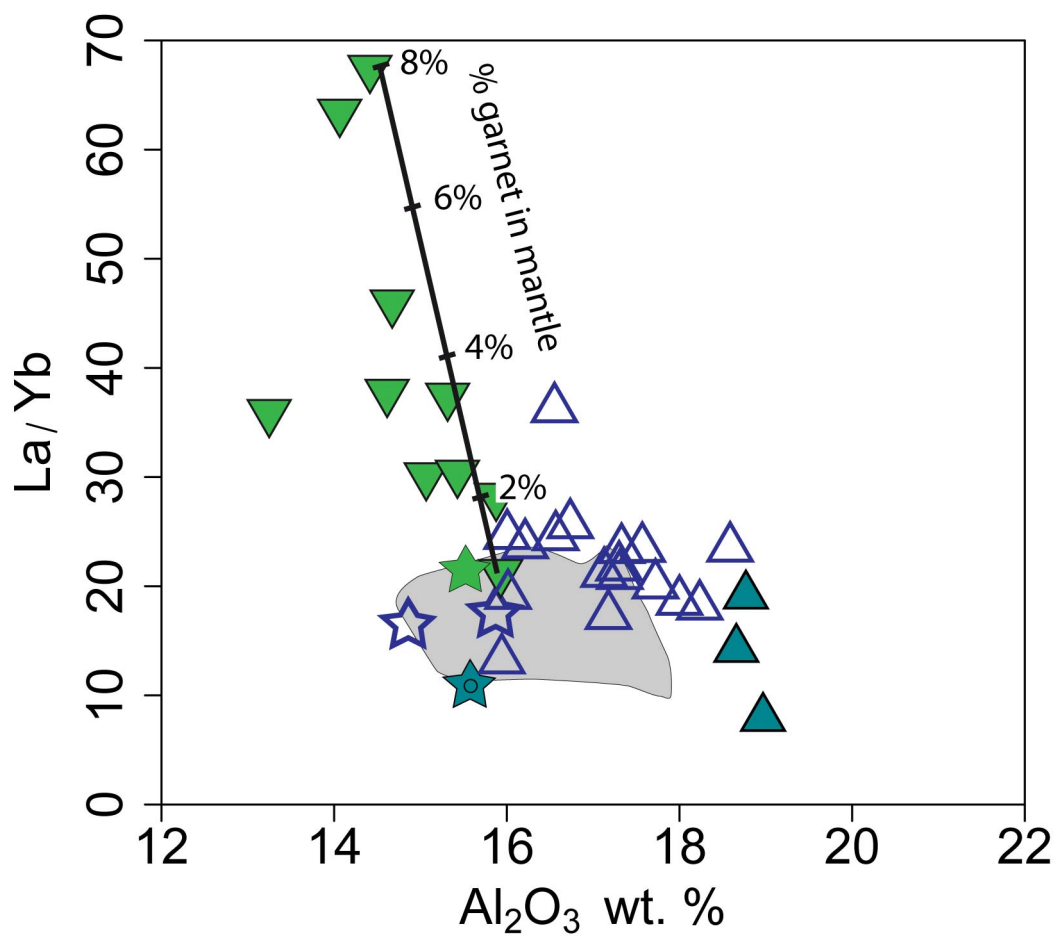


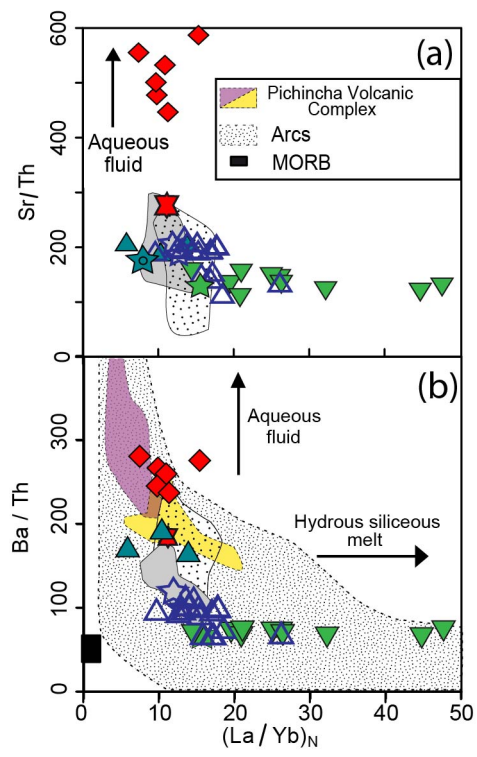


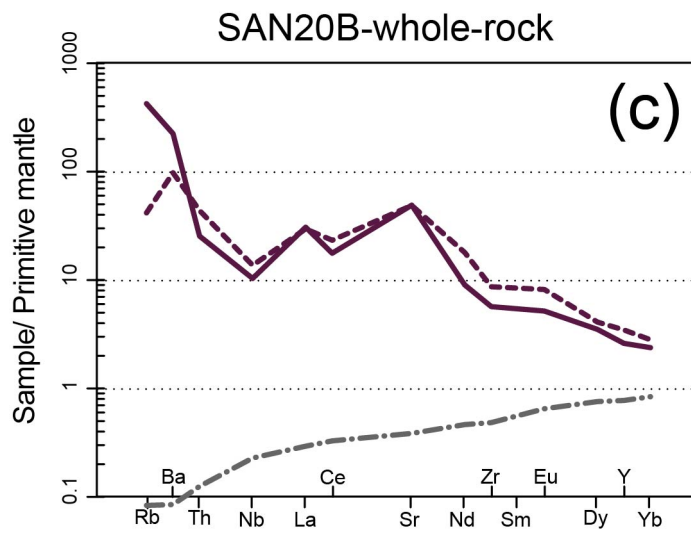
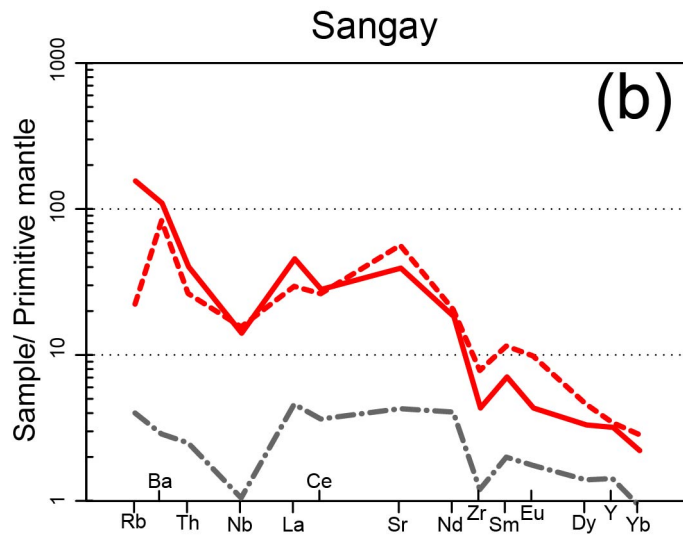
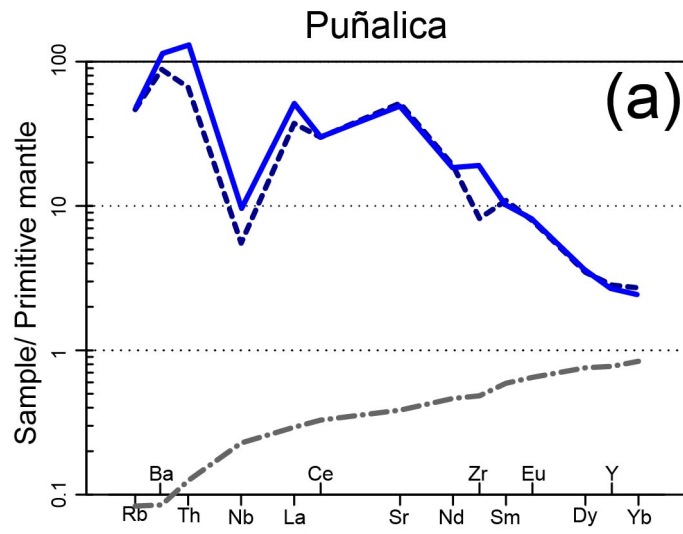


	Melt inclusions	WR
Puñalica Group	1 — CAR83A	[Shaded Grey Box]
	2 — RIO17A	
	3 — CAR96A	
Sangay	— SAN-20B	[Dotted Box]











**Table 1** Major, trace elements and volatile concentrations of olivine-hosted melt inclusions from Puñalica and Sangay lavas. Total given are the values. Major elements are the corrected values after wall olivine crystallization.

	<i>Sangay volcano</i>								<i>Puñalica volcano</i>					
	<b>SAN20B</b>								<b>CAR96A</b>					
	A	B	C	D	E	E1	F	G	AA	AB	AC	AE	AF	AG
SiO <sub>2</sub>	42.43	42.76	44.45	42.83	41.95	42.95	43.9	42.3	56.16	48.01	53.82	48.22	49.95	51.99
TiO <sub>2</sub>	1.53	1.7	1.48	1.36	1.8	1.65	1.45	1.41	0.41	0.75	0.53	0.67	0.68	0.88
Al <sub>2</sub> O <sub>3</sub>	19.11	18.44	16.59	17.09	18.53	18.82	18.02	18.75	15.32	14.41	15.88	14.67	13.25	15.93
FeO <sub>t</sub>	8.92	9.02	10.56	10.16	8.75	7.66	8.82	8.51	8.39	15.16	9.37	14.26	12.1	8.48
MnO	0.17	0.14	0.1	0.06	0.22	0.12	0.22	0.15	0.08	0.03	0.22	0.13	0.16	0.11
MgO	8.6	8.17	8.72	9.11	7.69	6.38	7.53	8.3	5.44	9.52	6.07	9.19	8.01	5.77
CaO	13.25	14.49	13.32	14.21	15.25	16.05	14.33	14.5	7.4	6.77	7.66	7.48	10	11.64
Na <sub>2</sub> O	4.24	3.73	3.35	3.55	4.25	4.62	4.17	4.28	4.48	3.48	4.17	3.5	3.83	3.6
K <sub>2</sub> O	1.32	1.12	0.99	1.02	1.19	1.31	1.13	1.22	1.97	1.53	1.91	1.54	1.72	1.36
P <sub>2</sub> O <sub>5</sub>	0.44	0.45	0.44	0.62	0.37	0.44	0.44	0.57	0.35	0.34	0.36	0.33	0.3	0.25
Total	94.56	94.75	93.82	95.3	96.39	98.36	96.41	92.92	99.27	99.15	99.68	98.35	97.6	99.3
H <sub>2</sub> O			3.17	2.6					0.09	0.1	0.09	0.1	0.07	0.07
CO <sub>2</sub> (ppm)			2776	6088					252	625	201	658	826	123
F (ppm)	913 <sup>b</sup>	843 <sup>b</sup>	720	627	963 <sup>b</sup>	1183 <sup>b</sup>	791 <sup>b</sup>	873 <sup>b</sup>	1626	1448	1492	1222	1388	1061
Cl (ppm)	2257 <sup>b</sup>	2052 <sup>b</sup>	1636	1776	2193 <sup>b</sup>	2227 <sup>b</sup>	1941 <sup>b</sup>	2213 <sup>b</sup>	5947	5813	5305	4958	5985	3928
S (ppm)	5417 <sup>b</sup>	3857 <sup>b</sup>	4029	3836	4519 <sup>b</sup>	4480 <sup>b</sup>	4552 <sup>b</sup>	5473 <sup>b</sup>	2467	3140	2829	3109	4805	2152
Sc	25.5	43.2	28.2	27.8	42.3		38.5		14.5	17.1	16.2	15	35.7	46.1
V	393.3	407.2	317.7	355.8	414.1		382.3		189.2	375.1	219.4	237.4	306.9	204.9
Rb	11.6	16.1	13.4	12.3	17.3		15.7		28.4	21.7	28.1	21.1	22.1	19.1
Sr	1356.4	1360.1	1123.4	1252.2	1420.3		1485		1459	1280.6	1332.7	1188.1	1351.4	1279.8
Nb	14.2	13.2	10.3	13.4	15.5		15.1		3.9	3.3	4.2	3.4	3.5	3.1
Ta	1.1	1.4	0.4	0.8	0.8		0.8		<0.192	<0.17	0.3	0.2	0.3	0.2
Ba	758.6	688.6	549	613.8	755.4		698.4		720.9	728.8	712.7	639.6	651.8	554.2
La	23.5	24.4	19.1	22	26.4		23.3		44	47.8	48.9	46.7	40.1	41.8
Ce	58.2	54.1	44.1	48.8	61.3		57.5		85.9	102.1	97.2	93.1	85	86.7
Pb	8.2	8.3	7.1	7.8			8.3		8.5	8.4	9.8	8.1	7.5	9.1
Nd	29.3	28.8	25.6	26.6	35.9		23.7		41.4	41.8	46.3	43.3	38.2	47.5
Sm	4.7	9	4.7	7.2	9.7		10		7.3	9.7	7	7.2	7.1	8
Zr	96.3	109.9	82.3	88.3	112.5		96.8		97.4	93.9	97.8	89.8	89.6	105.6
Eu	2	1.7	1.5	1.5	1.9		2		2	1.5	2	2	1.8	2.4
Gd	3.7	3.6	4.3	5.6	4.8		2.9		4.1	3	4.9	4.6	2.6	5.4
Dy	2.7	4	3.1	3.1	5.2		3.6		3.3	3.1	2.9	2.9	3.1	4.5
Yb	1.7	2.4	1.3	1.6	1.7		1.1		1.2	0.7	1.8	1	1.2	2.1
Th	2.8	2.5	2.1	2.5	3.2		2.5		10.5	10.4	10.4	10.2	9.5	8.5
U	1	1.3	0.8	1	0.8		0.3		3.3	3.5	3.3	3.4	2.9	2.6
Pr	6.4	6.9	5.9	6.5	7.5		7.8		9.8	11.1	10.9	10.7	9	10.8
Y	15.4	19.2	14.8	15.7	20		14.2		11.3	12.9	16.6	13.4	14.6	22.6
Lu	<0.19	<0.48	0.3	0.4	<0.32		<0.24		<0.174	0.3	0.3	0.2	0.4	0.4
Fo olivine	0.89	0.88	0.87	0.88	0.88	0.88	0.88	0.89		0.82	0.83	0.83	0.83	0.83
Ne	19.40	17.06	14.90	16.24	19.44	21.14	19.07	19.58		4.10		4.80	7.90	2.80
H <sub>v</sub>									8.65		1.27			

\* Samples with >10% of olivine crystallization correction. <sup>b</sup>F, Cl and F values from EMP, the other values for these volatiles are from SIMS. Ne normative composition

ε measured

**Table 1** continued

<i>Puñalica volcano</i>															
CAR96A							CAR113B								
AG1	AH		AH1	AI	AJ	AK	H	H1	I	J	J1	K*	K2	L	M
52.63	53.31	SiO2	53.27	49.16	51.12	48.3	48.05	47.52	52.35	48.17	49.88	53.62	46.26	49.77	50.01
0.63	0.43	TiO2	0.46	0.79	0.82	0.72	0.74	0.65	0.78	0.79	0.85	0.86	0.79	0.74	0.75
15.03	14.06	Al2O3	13.3	15.07	15.43	14.61	15.94	16.16	18.59	17.13	17.3	17.33	16.74	16.57	17.18
11.31	10.23	FeOt	10.85	12.82	9.46	12.81	12.72	12.92	6.91	11.01	9.71	9.36	14.38	10.63	10.45
0.16	0.13	MnO	0.06	0.18	0.18	0.13	0.04	0.16	0.11	0.17	0.11	0.21	0.08	0.07	0.22
7.63	6.74	MgO	7.33	8.43	6.27	8.45	9.22	9.35	4.91	8.02	7.04	6.11	8.77	7.68	7.36
6.14	8.67	CaO	8.68	8.36	10.71	9.32	8.53	8.74	9.74	9.78	9.65	6.88	7.88	9.27	9
3.95	4.14	Na2O	3.98	3.23	4.14	3.69	3.2	3.05	4.47	3.23	3.63	3.75	3.36	3.6	3.27
2.06	1.87	K2O	1.63	1.75	1.67	1.65	1.26	1.24	1.84	1.36	1.55	1.51	1.31	1.57	1.45
0.47	0.42	P2O5	0.45	0.21	0.2	0.3	0.29	0.21	0.31	0.34	0.28	0.37	0.44	0.1	0.31
99.52	99.46	Total	98.57	100.68	97.48	97.92	96.62	96.55	98.18	95.04	95.23	98.99	101.04	97.62	97.89
	0.07	H2O			0.07	0.06	1.63		0.33	2.35	3.07				1.98
	308	CO2 (ppm)			296	512	2053		262	802	376				645
2187 <sup>b</sup>	1194	F (ppm)	1412 <sup>b</sup>	596	950	922	503		624	518	699		655 <sup>b</sup>	673	483
5418 <sup>b</sup>	5629	Cl (ppm)	5252 <sup>b</sup>	3460	5458	4927	4021		5187	4598	4037		4137 <sup>b</sup>	5861	4318
2590 <sup>b</sup>	4434	S (ppm)	4362 <sup>b</sup>	1151	4331	4751	3818		1959	4701	6020		1635 <sup>b</sup>	4396	4271
	34.7	Sc		29.6	31.9	27	21.4		20.4	23.1	19.9	16	22.1	21.6	20.5
	173.1	V		274.5	190.5	240.9	216.2		183.2	216.4	214.2	166.3	251.8	199.8	206.6
	24.6	Rb		23.6	23.5	22.9	21		30.8	22.6	17.8	25.3	22.9	24.6	21.3
	1290.5	Sr		919.1	1298.8	1240.6	1129.3		1487.1	1228.6	1118	1021.5	935.8	1257.7	1110.7
	3.6	Nb		3.4	3.4	3.3	3.6		4.6	3.4	2.7	3	3.6	3.8	3.2
	0.2	Ta		0.2	0.2	0.2	<0.20		0.2	0.2	0.1	0.1	<0.22	<0.120	0.2
	700.5	Ba		558	611.1	633.2	571.9		732.4	583.9	507	3275.6	620.8	626.6	527.7
	50.5	La		41.8	38.9	44.7	28.9		37.4	31	31.5	26.3	44.1	30.4	26.5
	98.9	Ce		84.8	78	87.2	58.2		73.7	61.9	63.7	49.2	82.8	63.1	54.6
	8.6	Pb		5.5	7.9	7.7	8		10.1	8.2	6.2	6.3	7.9	9.4	7.5
	45.4	Nd		41.2	36.9	41.2	29.4		33.3	30.2	30.8	24.3	39.5	29	26.2
	7.4	Sm		7.3	6.5	7	4.1		5.8	5.1	4.8	4.3	6.1	5.9	4.9
	100.1	Zr		92.8	86.1	88.9	77		98.6	77.3	70.6	66.8	83.1	82.5	72.3
	1.8	Eu		1.8	1.5	1.8	1.6		1.4	1.4	1.5	1.2	1.4	1.4	1.2
	4.5	Gd		5.6	4	4.5	4.2		3.9	3.8	3.3	3	4	4.2	3.1
	3.3	Dy		3	3.2	2.7	2.6		2.9	2.6	2.5	2	1.8	2.6	2.4
	0.8	Yb		1.4	1.3	1.2	2.2		1.6	1.5	1.4	1.1	1.7	1.2	1.5
	11.3	Th		8.9	8.8	9.7	6		7.7	6.4	7.6	5.3	8.3	6.2	5.7
	3.5	U		3	2.8	3	1.9		2.6	1.9	2.2	1.7	3.1	1.9	1.7
	11.4	Pr		9.7	9	10	6.8		8.4	7.3	7.4	6	10.4	7.4	6
	14	Y		14	15.1	14	13.2		15.1	13.5	12.2	11.6	14.5	14	12.3
	0.2	Lu		0.2	0.2	0.2	<0.182		0.2	0.2	0.2	0.2	0.3	0.2	0.2
0.83	0.83	Fo olivine	0.83	0.83	0.83	0.83	0.84	0.84	0.85	0.84	0.84	0.83	0.83	0.85	0.84
	2.00	Ne	0.5	3.59	7.23	8.55	3.69	4.28	5.56	4.97	4.67		6.13	5.21	1.22
3.09		Hy										18.03			

and Hy are CIPW



**CAR83A**

Z	BA	BB	BC*	BD1
52.87	54.59	54.29	53.51	55.25
0.81	0.84	1.05	0.91	0.98
18.02	18.97	19.7	18.77	18.66
6.97	6.18	5.43	7.14	5.58
0.07	0.07	0.24	0.1	0.07
5.3	4.28	3.99	4.97	3.94
9.8	8.59	9.35	8.18	8.21
4.32	4.85	4.27	4.67	5.26
1.7	1.5	1.38	1.43	1.86
0.15	0.14	0.3	0.32	0.18
99	101.6	99.6	100.6	102.2
	0.06			0.11
	51			4307
1008 <sup>b</sup>	439	558 <sup>b</sup>	533 <sup>b</sup>	504
5717 <sup>b</sup>	1533	1625	1352 <sup>b</sup>	1948
2829 <sup>b</sup>	1571	609	1248 <sup>b</sup>	1562
	21.4		17.6	16.6
	205.4		180.4	201.6
	29.9		28.6	33.8
	584.6		562.6	584.8
	4		3.6	4.1
	<0.211		0.3	0.3
	483		453.8	597.1
	12.1		11.4	12.7
	25.9		25.7	29.1
	7.9		5.9	7.4
	13.5		13.9	13.9
	2.9		2.3	4.2
	88.8		83	89.3
	0.9		0.9	0.9
	3.6		2.3	2
	2.9		2.2	2.6
	1.5		0.6	0.9
	2.8		2.8	3.1
	1.1		1	1.2
	3.6		3.2	3.4
	11.5		10.3	10.6
	0.2		0.1	<0.19
0.86	0.83	0.84	0.83	0.84
4.08	1.32		0.94	3.03
		5.78		

**Table 2** New whole-rock data from Puñalica volcano. The remaining whole-rock data for Puñalica are from Schiano et al. (2010). All Sangay whole-rock used in this paper are from Monzier et al. (1999). SAN20B whole-rock sample is shown for reference.

Puñalica volcano																
	RIO17A	RIO 18bis	RIO 20bis	CAR-01F	CAR-09G	CAR-09J	CAR-13F	CAR-26C	CAR-59A	CAR-59B	CAR-59B bis	CAR-59D	CAR-71	CAR 79A	CAR 80	CAR 83A
SiO <sub>2</sub>	56.55	54.98	56.72	55.60	59.48	55.73	56.19	58.27	58.60	55.22	55.13	59.68	55.11	56.01	58.27	58.36
TiO <sub>2</sub>	0.74	0.76	0.75	1.04	0.78	1.04	0.92	0.85	0.78	0.75	0.74	0.75	0.80	0.75	0.76	0.76
Al <sub>2</sub> O <sub>3</sub>	14.85	16.23	15.47	17.96	16.97	17.87	17.23	16.26	17.19	16.78	16.77	16.29	17.30	15.46	15.63	15.59
FeO <sub>t</sub>	7.14	7.38	7.01	7.44	5.96	7.55	7.18	6.55	6.47	7.22	7.19	6.15	7.44	7.10	6.72	6.64
MnO	0.12	0.12	0.11	0.13	0.10	0.13	0.12	0.11	0.10	0.14	0.14	0.10	0.14	0.13	0.11	0.11
MgO	7.48	6.02	6.99	4.53	3.80	4.33	5.24	5.51	4.96	5.84	5.82	4.84	4.92	7.10	6.31	6.21
CaO	8.24	9.22	7.87	7.59	6.34	7.76	8.10	6.82	6.63	8.54	8.59	6.57	8.94	8.45	7.23	7.22
Na <sub>2</sub> O	3.41	3.58	3.68	3.89	4.44	3.77	3.77	4.03	3.86	3.69	3.75	3.99	3.79	3.49	3.69	3.77
K <sub>2</sub> O	1.26	1.45	1.21	1.59	1.89	1.57	1.01	1.40	1.20	1.55	1.62	1.42	1.34	1.31	1.11	1.17
P <sub>2</sub> O <sub>5</sub>	0.21	0.25	0.20	0.24	0.24	0.26	0.24	0.21	0.21	0.26	0.25	0.20	0.22	0.20	0.18	0.17
Total	99.65	99.56	99.41	100.12	100.06	100.10	99.37	100.41	100.05	100.47	100.04	99.35	100.96	99.90	99.98	100.14
Sc	20.20	25.68	19.89	18.61	14.55	18.62	24.06	17.19	15.84	23.68	24.17	15.57	25.55	23.69	20.09	19.41
V	184.00	211.44	185.91	206.76	160.92	208.94	208.03	173.05	159.84	203.50	196.73	159.22	226.67	190.40	172.09	172.74
Rb	21.50	19.35	18.69	39.09	36.44	37.71		27.35	31.03	21.45	30.19	38.48	25.92	23.44	21.54	23.53
Sr	910.00	1140.35	857.69	617.35	636.47	599.76	718.00	629.20	671.40	1136.62	1158.32	636.99	1133.55	922.83	547.22	558.13
Nb	3.40	4.31	4.11	5.95	5.36	6.12		4.46	3.94	3.95	4.07	3.94	3.55	3.70	3.61	4.45
Ba	525.00	612.44	488.73	688.48	857.12	738.29	472.00	592.16	632.32	660.61	665.55	601.98	551.44	546.09	415.31	442.94
La	20.50	33.68	19.23	16.42	16.30	15.16		16.74	20.52	34.43	33.88	20.24	21.61	21.93	11.72	12.41
Ce	43.00	65.31	36.77	32.19	33.12	33.26		33.28	40.02	65.91	65.07	37.31	42.71	43.41	25.13	25.56
Nd	22.00	31.30	19.58	18.76	17.09	18.13		17.26	21.29	32.36	32.41	20.53	23.22	22.34	13.69	13.87
Sm	4.35	5.72	3.71	4.24	3.52	4.12		3.82	3.81	5.56	5.75	3.78	4.30	4.29	2.98	2.97
Zr	95.00	97.50	93.38	120.92	122.20	126.08	106.73	102.97	105.47	93.38	88.33	100.92	88.13	95.21	94.43	98.07
Eu	1.15	1.46	1.17	1.17	0.97	1.17		1.00	1.11	1.48	1.51	1.11	1.22	1.25	0.86	0.92
Gd	3.50	3.93	2.85	4.16	2.93	3.77		3.37	3.46	4.16	4.01	3.12	3.58	3.28	2.61	2.78
Dy	2.45	2.96	2.38	3.19	2.29	2.93		2.16	2.12	2.94	2.92	2.13	2.86	2.57	2.29	2.30
Yb	1.24	1.60	1.13	1.58	1.19	1.55		1.04	0.89	1.58	1.61	0.89	1.63	1.33	1.07	1.12
Th	4.40	7.75	4.28	4.57	3.73	3.42		4.23	6.10	7.68	7.73	5.62	4.07	5.11	3.06	3.15
Y	12.90	17.12	12.82	18.03	13.59	18.29	16.35	12.06	10.62	16.60	16.76	10.85	17.54	14.62	12.16	12.83

ck data **Table 2 continued**

<b>Puñalica volcano</b>												
CAR-87		<b>CAR-113B</b>	CAR-88	CAR-89	<b>CAR-96A</b>	CAR-97	CAR-98	CAR-100	CAR-102	CAR-107	CAR-112	CAR-114A
58.13	SiO <sub>2</sub>	54.91	58.38	54.64	55.03	55.20	56.65	55.02	54.79	55.26	54.55	54.85
0.83	TiO <sub>2</sub>	0.74	0.82	0.72	0.71	0.72	0.78	0.72	0.79	0.78	0.79	0.79
16.33	Al <sub>2</sub> O <sub>3</sub>	15.88	16.39	15.35	15.52	15.61	16.28	15.81	17.39	17.65	17.35	17.32
6.82	FeO <sub>t</sub>	7.51	6.80	7.51	7.52	7.46	7.11	7.37	7.67	7.76	7.90	7.82
0.11	MnO	0.14	0.10	0.14	0.14	0.14	0.12	0.13	0.14	0.14	0.14	0.14
5.43	MgO	6.70	5.11	7.17	6.51	6.77	5.74	6.56	4.92	4.47	4.93	4.98
6.87	CaO	9.06	6.88	9.51	9.57	9.02	8.15	9.25	9.21	8.60	9.14	9.05
3.90	Na <sub>2</sub> O	3.45	3.96	3.34	3.34	3.48	3.77	3.48	3.62	3.83	3.72	3.60
1.36	K <sub>2</sub> O	1.40	1.34	1.38	1.40	1.38	1.20	1.42	1.25	1.28	1.24	1.26
0.22	P <sub>2</sub> O <sub>5</sub>	0.23	0.21	0.24	0.25	0.23	0.21	0.23	0.23	0.23	0.23	0.19
100.28	Total	98.71	99.92	98.69	98.19	98.61	97.55	98.64	100.30	99.14	98.08	99.85
16.61	Sc	25.27	16.27	27.30	27.45	25.27	19.52	25.42	25.72	23.53	25.49	25.73
167.83	V	197.99	173.85	211.53	214.44	202.29	182.59	208.71	219.77	213.74	221.29	221.47
24.51	Rb	18.95	24.99	17.26	16.57	19.01	17.26	19.77	13.92	15.22	14.80	14.51
635.41	Sr	1078.28	591.80	1041.79	1043.17	1061.88	801.35	1083.97	1093.99	1098.95	1066.35	1091.83
5.29	Nb	2.52	4.55	3.35	2.54	2.72	3.20	3.10	2.72	2.23	2.98	2.63
602.37	Ba	556.73	546.74	528.03	539.78	535.64	489.74	551.01	512.95	555.05	501.10	520.76
15.27	La	26.30	14.59	30.30	33.99	26.93	17.34	27.78	19.86	20.06	19.29	20.37
31.57	Ce	51.56	29.30	57.73	65.04	51.93	36.54	53.56	37.25	36.21	39.07	37.10
16.91	Nd	26.35	16.31	28.99	31.71	26.22	19.11	26.91	21.04	21.52	21.25	20.98
3.92	Sm	4.70	3.50	6.00	5.65	5.18	4.13	5.24	3.99	4.48	4.40	4.40
110.55	Zr	93.26	115.19	104.79	100.71	98.39	95.27	98.30	104.15	98.28	97.84	101.02
1.09	Eu	1.30	0.95	1.42	1.49	1.24	1.09	1.28	1.21	1.18	1.09	1.18
3.36	Gd	3.87	3.29	3.90	4.28	3.71	3.72	3.86	3.54	3.78	3.90	3.54
2.32	Dy	2.71	2.43	3.04	3.02	2.82	2.60	2.81	3.00	3.07	2.96	3.14
1.05	Yb	1.48	1.00	1.54	1.57	1.51	1.20	1.52	1.61	1.72	1.69	1.57
4.11	Th	5.78	3.44	7.06	8.16	5.83	3.73	5.83	3.72	3.85	3.69	4.18
12.12	Y	16.09	12.01	15.96	16.70	15.63	13.53	16.05	16.66	17.97	17.20	15.97

<b>Sangay volcano</b>
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SAN20B
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50.28
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1.01
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14.80
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8.71
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0.15
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11.12
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8.92
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3.34
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1.32
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0.34
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98.78
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24.00
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220.00
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25.00
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970.00
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9.00
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644.00
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19.20
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39.00
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22.40
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91.00
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1.26
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3.50
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2.76
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1.24
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3.50
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14.90
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