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Late Cretaceous felsic intrusions in oceanic plateau basalts in SW Ecuador: markers of subduction initiation?

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Abstract

Felsic magmatic rocks (tonalites and trondhjemites) with calc-alkaline affinity were emplaced in SW Ecuador (Pascuales area; North Guayaquil) at ~87–89 Ma intruding the top

of the basalts of the Caribbean Large Igneous Province (CLIP), prior to the development of typical well-known island arcs from ~85-80 Ma onwards. A clear depletion of REE distinguishes the Pascuales felsic rocks from the more differentiated lavas of the Rio Cala Arc in Ecuador and from other Late Cretaceous arc-like felsic intrusives emplaced within the CLIP in Colombia and the Antilles. In addition, the Pascuales tonalites have very low K_2O (< 0.4 wt.%), TiO_2 (< 0.4 wt.%) and P_2O_5 (< 0.15 wt.%) contents compared to dacitic rocks of the Rio Cala Arc. In contrast, their geochemistry and their similar age suggest that the Pascuales tonalites are an equivalent of the Las Orquideas dacitic volcanic rocks. The Pascuales felsic rocks have the less radiogenic Nd compositions of the whole spectrum of Ecuadorian oceanic plateau rocks, nevertheless shearing similarities with some Totoras amphibolites. The geochemical characteristics of the Pascuales intrusives and Las Orquideas dacites are similar to those formed by hydrous partial melting of mafic protoliths. The dacitic magmas must have been in equilibrium with residual mineral assemblages largely dominated by amphibole + Fe–Ti oxides (no garnet). This requires two conditions: 1) low-pressure melting under high water content and 2) a source rock extremely depleted in minor incompatible elements (K, Ti, P, Y) and REE. These conditions are fulfilled by partial melting of mafic-ultramafic cumulates undergoing high temperature and shear deformation at the base of the oceanic plateau triggered by new basaltic intrusions. The Pascuales felsic rocks emplaced at the SW border of the oceanic plateau during its final stage of building; they can thus be related to asthenospheric upwelling during the initial stage of island arc magmatism.

1. Introduction

The Caribbean Large Igneous Province (CLIP; Fig. 1) is an oceanic terrane currently exposed in the Caribbean region and in northwestern South America. The CLIP mainly

extruded between 100 Ma and 88 Ma (e.g. Kerr et al., 2003; Luzieux et al., 2006; Sinton et al., 1998; Villagómez et al., 2011; Wattam and Stern, 2015), although significantly younger rocks up to circa 65 Ma have been observed in the Gorgona Island and Western Colombia (Serrano et al., 2011; Sinton et al., 1998). The origin of the CLIP is also debated with theories proposing an extrusion in a location close to the paleo-Galapagos hot spot (e.g. Duncan et al., 1984; Whattam and Stern, 2015) or an origin related to a different plume event (e.g. Boschman et al., 2014). The borders of the CLIP are characterized by plateau basaltic rocks and tonalitic magmatism, the latter being ascribed to the melting of the plateau or to incipient subduction processes (e.g. White et al., 1999; Wright and Wyld, 2011; Villagomez et al., 2011; Whattam and Stern, 2015; Weber et al., 2015). Because of its high buoyancy and thickness (between 8 and >20 km; Kerr et al., 2003) it is believed that the CLIP (and an associated island arc) accreted to the South American margin between 80 Ma and 65 Ma (Vallejo et al., 2009; Villagómez et al., 2011; Kerr et al., 2002a; Hughes and Pilatasig, 2002; Jaillard et al., 2009).

Rocks from the southern limit of the CLIP in SW Ecuador include: 1) basalts, dolerites and gabbros typical of plateau settings with ages ranging between 90 Ma and 85 Ma (Kerr et al., 2002a; Luzieux et al., 2006; Vallejo et al., 2009, 2006), an interval that coincides with the major pulse of CLIP magmatic activity and with the supposed plume-induced subduction initiation at the margins of the CLIP, and 2) Late Cretaceous intrusive and volcanoclastic deposits (with ages also roughly coincident with the suggested subduction initiation beneath the CLIP) that have geochemical affinities that may relate them to a juvenile subduction setting (see also the bachelors thesis of Macias, 2018). However, various works in southwest and central Ecuador (Allibon et al., 2008; Amórtegui et al., 2011; van Melle et al., 2008) suggest that similar geochemical characteristics may result from the partial melting of the base of the oceanic plateau. Farther north, in the Western Cordillera of Ecuador, La Portada

Unit assigned to the base of the Rio Cala island arc (Kerr et al., 2002a; van Thournout, 1991; Wilkinson, 1998) and the Pujilí Granite (PG in Fig. 2) have been ascribed to the oldest evidences of subduction beneath the CLIP in Ecuador at ~85 Ma (Vallejo, 2007; Vallejo et al., 2009).

In the SW Ecuadorian forearc region, the CLIP rocks crop out at the Chongón-Colonche Hills (CCH, Figs. 1 and 2). The CCH hills are defined by a major positive gravimetric anomaly probably related to crustal thinning (the crust is only ~7 km thick versus ~15 km in average in the forearc) and resulting mantle upwelling (Aizprua et al., 2020). Several small tonalitic, gabbroic and ultramafic bodies intrude the CLIP rocks close to the area where the CCH is buried westwards beneath the Plio-Quaternary sedimentary cover (Fig. 2; Pichler and Aly, 1983; Benitez, 1995; Eguez et al., 2017). These intrusions were poorly studied in the past and, in addition, most outcrops are now extensively covered by new civil constructions. Tonalitic intrusive bodies located near the town of Pascuales (Fig. 3A) have reported K-Ar ages of 73.3 ± 4.8 Ma (Pichler and Aly, 1983) similarly to other circa K-Ar 70 Ma cooling ages that can be arguably interpreted as a thermal cooling event related to the collision of the CLIP onto South America (e.g. Aspden and Litherland, 1992). To date, there are no published geochemical nor geochronologic constrains for the intrusive rocks located near the town of Pascuales, which is unfortunate because they might help unravel part of the youngest Cretaceous geodynamic processes that occurred in SW Ecuador. In this work we present the results of in situ LA-ICP-MS U-Pb dating on zircon and new petrographic, geochemical and isotopic analyses on felsic intrusions sampled near Pascuales (Fig. 3A), as well as new geochemical and isotopic whole rock analyses on the country basaltic rocks. These data allow us to chemically characterize a group of intermediate to felsic magmatic rocks with calc-alkaline affinity, which emplaced at ~87–89 Ma at the top of the CLIP basalts (i.e. prior to the development of Late Cretaceous island arcs). In this context, the new data

presented here is combined with previously published analyses for plateau and island arc suites in Ecuador (i.e., Las Orquideas Member, Rio Cala Arc, San Lorenzo Formation) and Colombia in order to discuss the possible origins of these arc-like rocks, as well as their relations with the country-rock oceanic plateau basalts and resulting geodynamic implications.

2. Geological context

The Andean chain in Ecuador shows two distinctive Eastern and Western Cordilleras in which topographic growth most likely took place during the last 75-70 Ma (Gutiérrez et al., 2019; Spikings et al., 2010; Witt et al., 2017). The basement of the forearc and Western Cordillera (WC) is made up of oceanic plateau basalts (herein referred as OPB) which were accreted to the continental margin of South America. These accreted terrains have been ascribed to the Piñón, Pallatanga, San Juan and Guaranda terranes, units or formations (Fig. 2; Hughes and Pilatasig, 2002; Jaillard et al., 2009; Kerr et al., 2002a; Mamberti et al., 2003; Vallejo et al., 2009). The definition of the nature, number and timing of accretion events has been one of the most debated topics in the Ecuadorian geology for the last 30 years. For some authors, a single Caribbean type accretion occurred between 75-65 Ma (Luzieux et al., 2006; Vallejo et al., 2009; Chiaradia, 2009) whereas other studies suggest multi-episodic oceanic accretions (some of them with no Caribbean affinities) at ~75 Ma, ~68 Ma and ~58 Ma, and even early Eocene (e.g. Feininger, 1987; Hughes and Pilatasig, 2002; Jaillard et al., 2009; Kerr et al., 2002a; Aizprua et al., 2019). The debate is mostly originated by differences in the subduction polarity and the age of some oceanic rocks ascribed to the San Juan Formation (see below). Accretional events are believed to represent one of the main driving factors for the generation of relief in the Ecuadorian Andes (Jaillard et al., 2009; Witt et al., 2017).

The Piñón Formation (Fm.) represents the mafic plume-related basement of the Ecuadorian forearc and is mainly composed of tholeiitic, massive and pillowed basaltic and basalt–andesitic lavas, locally intruded by dolerites and/or gabbroic stocks (e.g. Kerr et al., 2003; Reynaud et al., 1999). In the CCH, the top of the Piñón Fm. has been ascribed to the lower part of the Coniacian (i.e. ~90 Ma) based on planktic foraminifera and radiolarians collected in cherts intercalated between pillow lavas and on the age of the overlying Calentura Fm. (Ordoñez et al., 2006; van Melle et al., 2008; Velasco and Mendoza, 2003). Furthermore, a gabbro within the Piñón Fm. yielded a hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ plateau age of 88.8 ± 1.6 Ma (Luzieux et al., 2006). The CCH is defined by one of the most significant gravimetric positive anomalies in the Northern Andes which most likely resulted from significant crustal thinning (the crust is only ~7 km thick in the CCH) and related denudation and mantle upwelling (Aizprua et al., 2020).

In the Western Cordillera, the Pallatanga / Guaranda Unit (92–88 Ma, Fig. 2; Kerr et al., 2002b; Kerr et al., 2003), likely also a fragment of the CLIP, is petrographically and geochemically similar to the Piñón basalts and dolerites (Kerr et al., 2002a; Mamberti et al., 2003). To the east of the Western Cordillera (Fig. 2), cumulate peridotites and gabbros intruded by mafic and felsic dykes of the San Juan Unit crop out as tectonic slices entrained within the Late Cretaceous ocean-continent suture (Hughes and Bermudez, 1997; Fig. 2). This unit is either interpreted as the root of the Pallatanga Unit (Lapierre et al., 2000; Hughes and Pilatasig, 2002) or as a magmatic chamber within the oceanic plateau (Mamberti et al., 2004). A gabbro of the San Juan Unit (SJG in Fig. 2) yielded a zircon U-Pb age of 87.1 ± 1.6 Ma interpreted as the crystallization age (Vallejo et al., 2006), comparable to the 88.8 ± 1.6 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ age obtained from the Piñón hornblende gabbro by Luzieux et al. (2006). Similarly, in the Tortoras area (TA in Fig. 2) one amphibolite yielded an age of 84.7 ± 2.2 Ma ($^{40}\text{Ar}/^{39}\text{Ar}$ in hornblende interpreted as a cooling age following amphibolite facies metamorphism prior

to the accretion of the oceanic plateau (Vallejo et al., 2006). However, an age obtained from gabbroic units also ascribed to the San Juan unit yielded a Sm/Nd isochron of 123 ± 13 Ma (Lapierre et al., 2000); suggesting that these rocks represent an older eruptive phase of the plateau and most likely an older accretionary process. Indeed, Miocene transpressive faults crosscutting the Western Cordillera also exhumed mafic granulites and amphibolites with geochemical and Nd isotopic compositions characteristic of oceanic plateau basalts (Jaillard et al., 2004; Beaudon et al., 2005; Amortegui et al., 2011), which differ from the Pallatanga Unit and Piñón Fm. because they have Pb isotopic features similar to those of the Late Cretaceous intra-oceanic arc (Amortegui et al., 2011).

In SW Ecuador, the Piñón Fm. is mostly overlain by magmatic or volcanoclastic successions with island arc affinities ascribed to the Santonian Cayo and Campanian-Maastrichtian San Lorenzo Fms., the latest cropping out at the NE directed Coastal Cordillera (Lebrat et al., 1987; Luzieux et al., 2006; van Melle et al., 2008; Reynaud et al., 1999; Figs. 1 and 2). However, in the CCH to the west of Guayaquil, a thin layer of volcanic rocks referred to as the Las Orquideas (LO) Member is intercalated between the Piñón basalts and the Calentura and Cayo sedimentary and volcanoclastic deposits (Reynaud et al., 1999; van Melle et al., 2008). The LO Member is a 30 to 150 m thick lava sequences mainly composed of explosive, intermediate to dacitic products (Benitez, 1995; Reynaud et al., 1999; van Melle et al., 2008). Pelagic microfauna in interbedded limestones allowed attribution of the LO volcanism to the Middle Coniacian (~88 Ma; van Melle et al., 2008 and references therein). Despite the calc-alkaline signature of the LO rocks, van Melle et al. (2008) considered that their emplacement in a subduction setting was very unlikely mainly because the generation of arc magma at ~ 100 km depth and its ascent to the surface would require more than the observed ~2 Ma time interval between the end of plume activity and the eventual formation of the subduction zone (i.e. with respect to the 85 Ma Pujili granite). Furthermore, these authors

suggested that the small volume of the volcanic cover is atypical for an island arc setting. Instead, these authors proposed that the LO volcanic rocks were generated by partial melting of deep parts of the CLIP.

In the Western Cordillera, arc sequences developed on top of the oceanic plateau (Fig. 2), both before and after their accretion(s) onto the continent. The Rio Cala Group (Santonian to early Maastrichtian; Hughes and Bermúdez, 1997; Boland et al., 2000) and its tholeiitic Rio Cala island arc (66.7 ± 7.2 Ma, Vallejo et al., 2009) represents the oldest clear evidence of arc magmatism observed in the Western Cordillera, yet its original position may have been related to either westwards (e.g. Vallejo et al., 2009) or eastward (e.g. Jaillard et al., 2009) subduction prior to the main accretional period 75-65 Ma ago (Vallejo et al., 2009; Chiaradia, 2009). An older age of 85.5 ± 1.4 Ma (zircon LA-ICP-MS U-Pb age; Vallejo et al., 2006) was obtained for the Pujilí Granite, which occurs within a tectonic block within the continent - ocean suture, east of the Western Cordillera (PG in Fig. 2). The adakitic nature of the Pujilí Granite and some plume-like mineralogical and geochemical characteristics of the Late Cretaceous arc magmatism in SW Ecuador suggest a hot subduction zone, which possibly facilitated the incorporation of a mantle plume component in the arc magmas through assimilation and/or partial melting of the CLIP (Allibon et al., 2008; Vallejo et al., 2009). According to Whattam and Stern (2015), all Late Cretaceous magmatic events (i.e. post-100 Ma) in Southern Ecuador correspond to hybrid magmas with both plume and subduction zone contributions, with a progressive increasing amount of subduction-related magma in the hybrid plume-mantle source.

3. Sampling and analytical methods

197

198 Samples of this study were collected north of Guayaquil in the easternmost border of
199 the CCH (Fig. 2), near the town of Pascuales (Fig. 3A) where intrusions of felsic plutonic
200 rocks occur within ~2-4 km long ~ 1.5 km wide areas (red outlines in Fig. 3A). The best two
201 preserved outcrops show subhorizontal, ~5 m thick, layers of massive, greenish to grey pale
202 rocks affected by numerous orthogonal fractures. One of the outcrops (Fig. 3B) provided two
203 pieces of trondhjemites (GD001 and GD002) forming the lower layer, while three tonalite
204 pieces were sampled in the upper layer (GD003, CP601, CP024). A fourth trondhjemitic
205 sample (CP603) was collected in the second outcrop (Fig. 3C). Rocks surrounding the felsic
206 intrusions are medium to fine grained basalts and metabasalts showing variable degrees of
207 mylonitization and alteration. Locally, they are cross-cut by hornblende-filled shear zones,
208 and veinlets or microdykes composed of dioritic mineral assemblages (plagioclase,
209 magnesiohornblende and opaque minerals). Least altered volcanic mafic rocks were also
210 sampled at different locations (CP605, CP607, GD004; Fig. 3A). Mineral compositions of
211 selected samples were determined with a CAMECA SX100 electron microprobe with 4
212 wavelength-dispersive spectrometers at the Ecole Nationale Supérieure de Chimie in Lille
213 University. Analytical conditions were 15 kV acceleration voltage, 15nA beam current and a
214 peak counting time of 20s. Natural standards were used for the electron microprobe
215 calibration. Zircon U-Pb geochronology was conducted by in-situ laser ablation inductively
216 coupled plasma mass spectrometry (LA-ICP-MS) at the GeOHeLiS analytical platform
217 (Géosciences Rennes/OSUR, Univ. Rennes) using an ESI NWR193UC Excimer laser coupled
218 to a quadrupole Agilent 7700x ICP-MS equipped with a dual pumping system to enhance
219 sensitivity. Concordia ages and diagrams were generated using Isoplot/Ex (Ludwig, 2012).
220 Operating conditions are presented in Table S1. For a more detailed description of the
221 analytical protocol see Manzotti et al. (2015) and Witt et al. (2019). Whole-rock compositions

were obtained by fusion technique (lithium metaborate/tetraborate). Diluted solutions were analyzed for major oxides by Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES) and by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) for trace elements, at the Actlabs laboratory (Ontario, Canada) according to code 4Lithoresearch package. The international standards used for analytical control were BIR-1a (basalt), DCN-1 (dolerite), GBW 07113 (rhyolite), TDB-1 (diabase rock), DTS-2b (dunite), SY-4 (diorite gneiss), NCS DC86312 (rare earth ore) CTA-AC-1 (apatite concentrate). for further details, see <http://www.actlabs.com>.

Radiogenic isotope ratios of Sr ($^{87}\text{Sr}/^{86}\text{Sr}$), Nd ($^{143}\text{Nd}/^{144}\text{Nd}$) and Pb ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$) were measured at the Department of Earth Sciences (University of Geneva, Switzerland). The method is described in detail in Chiaradia et al. (2020). Briefly, 100 to 120 mg of whole rock powder were dissolved in concentrated HF and HNO₃. Samples were dried and re-dissolved in concentrated HNO₃ and dried again. Sr, Nd and Pb were then separated using cascade columns with Sr-Spec, TRU-Spec and Ln-Spec resins according to a protocol modified from Pin et al. (1994). The material was finally redissolved in 2% HNO₃ solutions and ratios were measured using a Thermo Neptune PLUS Multi-Collector ICP-MS in static mode. Long-term (>2 years) reproducibility of SRM987 (McArthur et al., 2001), JNdi-1 (Tanaka et al., 2000) and SRM981 (Baker et al., 2004) standards are 10 ppm (1SD) for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$, 0.0048‰ for $^{206}\text{Pb}/^{204}\text{Pb}$, 0.0049‰ for $^{207}\text{Pb}/^{204}\text{Pb}$ and 0.0062‰ for $^{208}\text{Pb}/^{204}\text{Pb}$. $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and Pb isotope ratios were corrected for external fractionation (due to a systematic difference between measured and accepted standard ratios) by a value of -0.021‰, +0.051‰ and +0.36‰ amu respectively. Total procedural blanks were <500 pg for Pb and <100 pg for Sr and Nd which are insignificant compared to the amounts of these elements purified from the whole rock samples investigated.

4. Petrography and mineralogy

4.1. Felsic rocks

Samples CP601, CP024, GD003 are medium-grained tonalites composed of quartz (~27–32 vol.%), plagioclase (~50–55 vol.%) and green amphibole (~10–12 vol.%; supplementary Fig. S1A). Plagioclase and amphibole occur as euhedral-subhedral prismatic crystals, while quartz is mainly present in a granular mosaic texture enclosing the former minerals. Apatite, titanite, zircon and titanomagnetite are accessory minerals. Plagioclase grains are zoned with Ca-rich cores and Na-rich rims; their compositions range from $An_{55}Ab_{44}Or_1$ to $An_7Ab_{88}Or_4$ (average $An_{39.6}Ab_{59.0}Or_{1.4}$; $n = 27$). Dark green magnesiohornblende forms stubby, commonly twinned, prismatic crystals, locally replaced by actinolite. Minor amounts of epidote, chlorite and magnetite also occur as intergranular phases and as inclusions in the magnesiohornblende cores where they may represent former pyroxenes. Samples CP603 (Fig. S1B), GD001 and GD002 mostly consist of euhedral-subhedral albite ($Ab_{99\pm1}$; $n = 17$) and quartz in near equal amounts, and correspond to trondhjemites following the definition of Barker (1979). Textures are hipidiomorphic granular to granophyric (e.g., graphic intergrowths of quartz and albite forming almost 20 vol.% of the rocks). Primary mafic minerals (up to 7 vol.%, likely former amphiboles) are replaced by chlorite, Fe-oxides and epidote group minerals. Titanomagnetite \pm ilmenite, titanite and zircon occur as accessory phases.

4.2. Mafic rocks

4.2.1 Petrography

Sample CP605 (Fig. S1C) is a dark green, fine-grained, undeformed and homogeneous metabasite. Rare, euhedral to subhedral, clinopyroxene phenocrysts (400–600 µm in diameter; ~1 vol.%) are fully pseudomorphosed by green amphiboles. Groundmass is intersertal-intergranular, composed of skeletal plagioclase laths ($An_{41\pm 11}$; $n = 38$), clinopyroxene grains partially replaced by amphibole, and accessory ilmenite, titanomagnetite, apatite and pyrite. Sheaf-like radial clusters of plagioclase are also observed. Low-grade secondary minerals form less than 5 vol.% and are represented by chlorite, albite, epidote, titanite, biotite and magnetite. Sample CP607 (Fig. S1D) shows a cataclastic structure but has preserved undeformed parts with igneous texture that are large enough to be analyzed. Igneous texture is sparsely phyrlic (<1 vol.%) with ~1–2 mm sized, subhedral pseudomorphs of clinopyroxene phenocrysts fully replaced by brownish to dark green amphiboles. They have spongy cores enclosing groundmass and are surrounded by ~100 µm - thick corona also replaced by amphiboles whose shapes and color are similar to those in the cores but oriented differently. Groundmass is holocrystalline, medium-grained (400–600 µm), made of plagioclase laths partially albitized and clinopyroxenes replaced by amphibole, titanite and magnetite. Accessory ilmenite and titanomagnetite are widespread in groundmass. Other low-grade secondary minerals (< 5 vol.%) are albite, chlorite, magnetite, quartz, epidote group minerals and biotite. Sample GD004 (Fig. S1E) is a medium-grained (200–700 µm), isogranular basalt made of plagioclase, clinopyroxene and abundant, up to 150 µm sized crystals of ilmenite and titanomagnetite. Hydrothermal alteration is marked by replacement of plagioclase, pyroxene and Fe-Ti oxides by albite, diopside, epidote, titanite and crystallization of pyrite-chalcopyrite.

4.2.2. Mineral chemistry

Fresh clinopyroxenes (Table S2; Fig. 4A,B) have been only preserved in samples CP605 and GD004. In CP605 they are magnesian augites ($\text{En}_{49.7\pm0.9}\text{Wo}_{39.4\pm0.9}\text{Fs}_{11.0\pm0.8}$; $n = 16$) which show variable Al_2O_3 contents (2.21 ± 0.36 wt.%) negatively correlated with Mg# [= molar $\text{Mg}/(\text{Mg} + \text{Fe}_{\text{tot}}) = 83\text{--}80$]. Although somewhat scattered, GD004 clinopyroxenes are augites ($\text{En}_{48.0\pm0.5}\text{Wo}_{37.1\pm0.6}\text{Fs}_{14.9\pm0.7}$; Mg# 78–75; $n = 36$) slightly poorer in Al_2O_3 (1.93 ± 0.14 wt.%).

Primary plagioclase compositions range from An_{59} to An_{24} ($\text{An}_{42\pm11}$; $n=47$) in CP605 and from An_{75} to An_{25} ($\text{An}_{51\pm16}$; $n = 48$) in CP607. In both samples secondary albitic compositions ($\text{An}_{9\pm3}$ in CP605; $\text{An}_{10\pm2}$ in CP607) forming 12–15% of the analytical set are separated from the primary compositions by a compositional gap. In GD004 all the plagioclases are albitized.

Amphiboles are the major mafic phases in CP605 and CP607 and are absent in GD004. Their compositions calculated according to the 13-cations method (e.g. Leake et al., 1997; Ridolfi et al., 2010) are listed (Table S2). They are Ti-poor ($\text{Ti} \leq 0.1$ apfu), Mg-rich [$\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) = 0.6\text{--}0.8$] calcic ($[\text{Ca}]_{\text{B}} = 1.7\text{--}1.9$ apfu) amphiboles showing a large range of compositions (Fig. 4C). Aluminous end-member compositions ($^{\text{IV}}\text{Al} = 1.6\text{--}2.0$ and $[\text{Na} + \text{K}]_{\text{A}} = 0.46\text{--}0.58$) occur as small, relic inclusions within the less aluminous amphiboles (Fig. S1F). Their compositions are transitional between tschermakitic pargasite ($^{\text{IV}}\text{Al} \geq 0.5$; $[\text{Na} + \text{K}]_{\text{A}} < 0.5$) and magnesiohastingsite ($^{\text{IV}}\text{Al} \geq 1.5$; $[\text{Na} + \text{K}]_{\text{A}} \geq 0.5$) (Fig. 4D), indicating crystallization at high temperature (e.g., ≥ 850 °C, Ridolfi et al., 2010 and therein references). Their low Ti contents suggest a metamorphic / hydrothermal origin (e.g. Coogan et al., 2001;

Gillis et al., 2001, Ridolfi and Renzulli, 2012 for a review). Furthermore, a small amount of chlorine was detected with the EDS (energy dispersive spectroscopy). Compositions of the other amphiboles vary from magnesiohornblende to actinolitic hornblende. In both samples, the wide compositional range, with decreasing ^{IV}Al (down to 0.5) positively correlated with decreasing alkali contents ($[Na + K]_A$ down to 0.02) (Fig. 4D), reflect crystallization at decreasing temperatures in lower to upper amphibolite facies conditions (~850–450°C, Anderson and Smith, 1995; Gillis and Roberts, 1999; Helz, 1982). Replacement of the pyroxenes thus started at high temperature under static conditions, likely reflecting seawater/hydrothermal alteration/metamorphism that occurred shortly after eruption, when the basalts were still hot. Amphiboles in veins crosscutting the basalts and associated with cataclasis are low-Al hornblende and actinolite.

5. U–Pb dating of zircon

Two tonalites (CP024 and CP601) and one trondhjemite (CP603) were selected for U–Pb dating. Results are reported in Table S3 and plotted in Fig. 5. Zircons vary from irregular with few developed faces to anhedral (Fig. S1G). They show little or no cathodoluminescence. For sample CP024, 18 analyses were performed on 18 different zircon grains. Plotted in a Tera-Wasserburg diagram (Fig. 5A), fifteen of them are concordant within error (plain line ellipses in Fig. 5A and in bold in Table S3) while three have a discordancy between 5 and 9% (dashed-line ellipses in Fig. 5A). These fifteen concordant data yield a concordia date (as of Ludwig, 1998) of 89.6 ± 2.0 Ma (MSWD = 1.2) identical within error with the $^{206}Pb/^{238}U$ weighted date of 89.7 ± 0.6 Ma (MSWD = 0.75; $n = 6$). The position of the three remaining discordant analyses is attributed to the presence of a slight common Pb component together with a very small Pb loss (at least for analyses 25120314 and 30120314,

see Table S3 and Fig. 5A). Sample CP601 was collected on the same outcrop as sample CP024. In this case all the seventeen analyses are discordant (Fig. 5B). This discordancy is interpreted as the sign for the presence of initial (common) Pb in the analyzed zircon grains. If an isochron is anchored to a $^{207}\text{Pb}/^{206}\text{Pb}$ initial value of 0.84 (calculated following then Stacey and Kramers (1975) Pb evolution model for an age of 90 Ma), the resulting lower intercept yields a date of 87.2 ± 1.3 Ma (MSWD = 4.6; n = 17). Thirteen zircon analyses from sample CP603, plot in a concordant to discordant position (Fig. 5C) revealing different amount of initial (common) Pb in the grains. Five analyses are concordant within error (grey ellipses in Fig. 5C and in bold in Table S3) yield a concordia date of 86.5 ± 2.3 Ma (MSWD = 4.8; n = 5) while the whole set of data return a lower intercept date of 85.3 ± 1.0 Ma (MSWD = 2.2; n = 13) if the isochron is anchored to a $^{207}\text{Pb}/^{206}\text{Pb}$ initial value of 0.84. In the light of these data, we conclude that these felsic intrusives were emplaced 87-89 Ma ago.

6. Elemental geochemistry

Whole rock major element analyses were performed on five felsic and three basaltic samples. Results are presented in Table 1 and plotted in Fig. 6–9 along with analyses of Late Cretaceous (pre-collision) magmatic rocks from southwestern Ecuador for comparison (see Fig. 2 for their spatial distributions/positions). All compositions are recalculated as volatile-free and summing to 100%.

6.1. Felsic rocks

Consistent with their mineralogy, the five analyzed samples plot as tonalites (CP601 and GD003) and trondhjemites (CP603, GD001, GD002) on Barker et al. (1979)'s Ab-An-Or diagram (Fig. 6). Loss on ignition (LOI) vary from 0.85 to 1.98 wt.%, in agreement with minor hydrothermal alteration and/or weathering. The abundances in major and trace elements are plotted against silica in Figs. 7 and 8, respectively. SiO₂ contents range from 66.5–69.8 wt.% at 2.5–2.7 wt.% MgO in the tonalites to 78.0–80.1 wt.% at 0.3–0.6 wt.% MgO in the trondhjemites. The transition from tonalite to trondhjemite is marked by decreases of Fe₂O₃* (~6.3 to 1.5–3.7 wt.%), Al₂O₃ (~13.6 to 11.3 wt.%), CaO (~4.7 to 1.0 wt.%), P₂O₅ (~0.07 to 0.03 wt.%), V (127 to 12 ppm, not shown) and Sr (~216 to 64 ppm). Inversely, Na₂O (~4.1 to 5.2 wt.%), La (~4.4 to 5.6 ppm), Zr (~54 to 91 ppm), Nb (~1.7–2.2 ppm) and Th (~0.6–1.0 ppm) increase slightly. Both the tonalitic and trondhjemitic samples are characterized by extreme depletions in REE (3.7–6.2 ppm La; 0.65–0.85 ppm Yb) and Y (4.8–7.4 ppm). Compared to more differentiated lavas of the Rio Cala Arc, the Pascuales tonalites are distinctly depleted in K₂O (< 0.3 wt.%), TiO₂ (< 0.3 wt.%) and P₂O₅ (< 0.05 wt.%) contents and are 21–26% more depleted in REEs and Y at 68–70 wt% SiO₂. On the other hand, they are similar to the LO volcanic rocks having more than 57 wt.% SiO₂ (except one LO dacite which is enriched in K₂O).

Chondrite-normalized (CN) REE abundances (Fig. 9A,B) of the Pascuales felsic rocks like those of LO dacites (≥ 63 wt.% SiO₂) exhibit flat HREE concentrations ($\text{Er/Y}_{\text{CN}} = \sim 1.0$ –1.1) followed by moderate enrichments in the more incompatible REE ($\text{La/Sm}_{\text{CN}} = 1.5$ –2.0 and 1.7–2.2 in tonalite and dacite, respectively; $\text{La/Yb}_{\text{CN}} = 3.6$ –4.7 in both rock types). In contrast, the Ho/Yb_{CN} ratios in trondhjemite decrease progressively from ~ 1.0 in GD001 to 0.7 in GD002, together with increasing enrichments in LREE relative to MREE ($\text{La/Sm}_{\text{CN}} = 2.7$ –4.0) and HREE ($\text{La/Yb}_{\text{CN}} = 4.4$ –6.5); these chemical features are especially marked in the trondhjemitic sample GD002. The tonalites show moderate depletions in Eu relative to

adjacent REE ($\text{Eu}/\text{Eu}^* = 0.80\text{--}0.86$), while the trondhjemitic GD002 displays a pronounced positive Eu anomaly ($\text{Eu}/\text{Eu}^* = 1.43$), reflecting plagioclase fractionation for the former and accumulation of sodic plagioclase for the latter. The other trondhjemitic samples lack any Eu anomaly.

On multi-element plots normalized to the Primitive Mantle (PM; Fig. 9C), all the silica-rich samples display subduction-like geochemical signatures characterized by negative Nb anomalies. However, Nb depletions relative to La are significantly less pronounced in the Pascuales intrusives and LO dacites ($\text{Nb}/\text{La}_{\text{PM}} = 0.37 \pm 0.03$ and 0.48 ± 0.05 , respectively) than in the silicic lavas from the Rio Cala Arc ($\text{Nb}/\text{La}_{\text{PM}} = \sim 0.20 \pm 0.01$) and in the Pujili Granite ($\text{Nb}/\text{La}_{\text{PM}} = 0.10$). Another major difference is the positive anomalies in Zr and Hf observed in the Pascuales tonalites and LO dacites ($\text{Zr}/\text{Sm}_{\text{PM}} = 1.3\text{--}1.5$ and $1.5\text{--}2.8$, respectively) versus negative Zr and Hf anomalies in Rio Cala andesites and dacites ($\text{Zr}/\text{Sm}_{\text{PM}} = \sim 0.8 \pm 0.2$) and in Pujili Granite ($\text{Zr}/\text{Sm}_{\text{PM}} \sim 0.4$). In the trondhjemitic samples, Zr and Hf spikes are more pronounced ($\text{Zr}/\text{Sm}_{\text{PM}} = 2.2\text{--}3.8$) than in the tonalites, the trondhjemitic sample GD002 having the highest ratio. Plots of REE, Th, Y and Zr against Nb, a highly incompatible trace element and the least mobile during hydrothermal and/or seawater alterations (Pearce, 2014), show that Pascuales and LO volcanic rocks define trends with slopes intermediate between those of the island arc lavas and the OPB (Fig. S2).

In summary, the Pascuales felsic intrusions have tonalitic and trondhjemitic compositions, characterized by extremely low K_2O , TiO_2 , P_2O_5 and REE concentrations; they are moderately depleted in Nb relative to La and enriched in Zr and Hf relative to Sm. These chemical features clearly distinguish the Pascuales felsic compositions from the silicic volcanic rocks of the Rio Cala Arc, but are shared by the LO dacitic samples.

6.2. Mafic rocks

418

419 LOI vary from 1.6 wt% in CP605 through 2.2 wt% in CP607 to 3.9 wt% in GD004
420 (Table 1). On an anhydrous basis, all samples have basaltic compositions ($\text{SiO}_2 = 50.8\text{--}51.7$
421 wt%, $\text{MgO} > 5$ wt%). CP605 and CP607 have near primitive compositions ($\text{MgO} = 7.4\text{--}8.1$
422 wt%, $\text{Cr} = 160\text{--}190$ ppm, $\text{Ni} = 100\text{--}110$ ppm), whereas GD004 has a more differentiated
423 composition, as shown by lower MgO (5.1 wt%), Cr (20 ppm) and Ni (40 ppm) contents and
424 higher TiO_2 , V and incompatible trace elements, such as REEs, Y, Nb, Th, Zr and Hf (Table
425 1).

426 In the Harker diagrams (Figs. 7 and 8) the three analyzed basaltic samples fall
427 systematically within the compositional fields of the Ecuadorian OPB and, in particular, their
428 compositions are similar to those of the Piñón basalts previously sampled in the CCH
429 (Reynaud et al., 1999; van Melle et al., 2008). Plotted against Nb, the concentrations in
430 alteration-mobile incompatible elements (Sr, Rb and Ba) also are within the ranges of the
431 variably altered Ecuadorian OPB (Fig. S2). In contrast, U concentrations in CP605, and to a
432 lesser extent in CP607, plot above the Ecuadorian OPB trend, suggesting U gain during
433 alteration.

434 On a chondrite-normalized REE diagram (Fig. 9D), samples CP605 and CP607 plot in
435 the middle of the Ecuadorian OPB field at $\text{Yb}_{\text{CN}} = \sim 16$, whereas GD004 plots at $\text{Yb}_{\text{CN}} = \sim 29$
436 at the upper boundary among the most evolved OPB compositions. Samples CP605 and
437 GD004 display flat REE patterns ($\text{La}/\text{Yb}_{\text{CN}} = \sim 0.9$), while CP607 is slightly depleted in LREE
438 ($\text{La}/\text{Yb}_{\text{CN}} = \sim 0.6$). Samples CP607 and GD004 exhibit small negative anomalies in Eu
439 ($\text{Eu}/\text{Eu}^* = 0.87$ and 0.93 , respectively).

440 The Pascuales basaltic samples are significantly enriched in the most incompatible
441 elements ($\text{Nb} = 3.6\text{--}5.9$ ppm, $\text{Th} = 0.36\text{--}0.45$ ppm) with respect to N-MORB (Fig. 9E). The
442 values of $(\text{Nb}/\text{La})_{\text{N-MORB}}$ (1.1–1.7) and $(\text{Th}/\text{Nb})_{\text{N-MORB}}$ (1.5–2.1) are within the range of the

other Ecuadorian OPB (1.1–1.7 and 1.1–2.7, respectively) and within the range of the six CCH basalts previously published (1.1–1.4 and 1.2–1.9, respectively). Nb/U ratios (12–30) are lower than those in oceanic (49–50) and Ecuadorian (33–48) OPB, confirming U enrichment during alteration. Sample CP607 displays a strong positive anomaly in Sr ($\text{Sr}/\text{Sr}^* = 2.2$), whereas CP605 shows a smaller positive anomaly ($\text{Sr}/\text{Sr}^* = 1.3$), which are not correlated with higher Al_2O_3 and Sr values and likely reflects alteration. In contrast, the slight Sr depletion in GD004 ($\text{Sr}/\text{Sr}^* = 0.8$) is consistent with the small Eu anomaly, indicating minor plagioclase fractionation. In addition, Ti in GD004 is enriched relative to the adjacent REE, reflecting Fe-Ti oxide accumulation, in agreement with high Fe_2O_3 contents and evolution toward ferrobaltic composition.

In summary, the basaltic rocks collected in Pascuales are tholeiites with flat to slightly LREE depleted patterns, geochemically similar to the Late Cretaceous oceanic plateau basalts of the Piñón Fm. Samples CP605 and CP607 have moderately differentiated compositions, whereas GD004 have evolved toward a ferrobalt, which is consistent with the mineralogy. Although they crop out within a very restricted area (Fig. 3), the three basalts exhibit highly variable Nb/La ratios (~1 to 1.56), suggesting that they represent different OPB units, a heterogeneity typically observed in CLIP basalts (Kerr et al., 2002b, 2003).

7. Nd, Sr and Pb isotopic data

The three basaltic samples, one tonalite (GD003) and two trondhjemites (CP604 and GD001) have been analyzed for Sr–Nd and Pb isotopic compositions. Results are reported in Table 1 and plotted in Fig. 10; complete results are listed in Table S4. The basalts of this study have homogeneous ϵNd_i (+6.9 to +7.4) similar to two (out of three) previously

published basalts from the CCH and overlap the Nd–Sr isotopic fields of the CLIP and Late Cretaceous island arc volcanic rocks from Ecuador (Fig. 10A). Relatively high ($^{87}\text{Sr}/^{86}\text{Sr}$)_i ratios (0.70464–0.70472) are likely related to the seawater and hydrothermal alterations observed in thin sections. Nevertheless, the range of the Sr isotopic ratios for all samples is rather restricted, precluding any major alteration-induced modifications on the Sr isotopic system. The ($^{206}\text{Pb}/^{204}\text{Pb}$)_i and ($^{207}\text{Pb}/^{204}\text{Pb}$)_i values of the Pascuales basalts are high and slightly scattered (18.64–18.93 and 15.54–15.63, respectively) but still in the range of the Ecuadorian OPB with the exception of CP607 which has the lowest ($^{206}\text{Pb}/^{204}\text{Pb}$)_i and the highest ($^{207}\text{Pb}/^{204}\text{Pb}$)_i ratios (Fig. 10C). However, because of the very low values of their Nb/U ratios (12–29 versus 47 ± 10 in oceanic mantle, Hofmann, 1988), Pb isotopic data of the Pascuales basalts may not be meaningful, rather reflecting post-magmatic addition of U. Lead is also known to be mobile during alteration (Hauff et al., 2000b); but, in this study, its mobility cannot be evaluated because the concentrations are below the detection limit (<5 ppm). Pascuales felsic intrusions have relatively low ϵNd_i (+4.4 to +5.6), nevertheless similar to that of the CCH Piñón basalt Ca1 (+4.5) analyzed by Reynaud et al. (1999) and within the range of Late Cretaceous picrites and alkali basalts from Tortugal in Costa Rica ($\epsilon\text{Nd}_i = +6.9$ to +4.2; Hauff et al., 2000a; Trela et al., 2017) and the Beata Ridge in the Caribbean Sea ($\epsilon\text{Nd}_i = +5.2$ –+5.4; Hauff et al., 2000b) and also similar to some gabbro–wehrlite cumulate samples from the San Juan Unit (Mamberti et al., 2004; Lapierre et al., 2010). In the diagram ($^{143}\text{Nd}/^{144}\text{Nd}$)_i versus ($^{206}\text{Pb}/^{204}\text{Pb}$)_i Pascuales felsic rocks fall in the same field as Tortugal lavas, which is subparallel to that of the Galapagos (Fig. 10B). The tonalite GD003 and the trondhjemite GD001, collected in the same outcrop (Fig. 3B), are similarly radiogenically enriched in ($^{206}\text{Pb}/^{204}\text{Pb}$)_i and ($^{207}\text{Pb}/^{204}\text{Pb}$)_i with respect to the tonalite CP603 which was sampled in a nearby outcrop (Fig. 3C) suggesting post-magmatic, small-scale variations. The more radiogenic Pb isotopes in GD001 and GD003 may reflect assimilation of minor amounts

of sediment which were interbedded in the basaltic crust. Small variations among the three felsic rocks also affect the Sr isotopic ratios, likely in relation with late-stage hydrothermal fluids.

In summary, the isotopic values for both Pascuales basaltic and felsic rocks are within the range of Ecuadorian OPB and volcanic rocks of other parts of the Caribbean oceanic plateau. However, with ϵNd_i ranging between +4.4 and +5.6 the felsic plutonic rocks plot among the less radiogenic Nd compositions and have more radiogenic Sr and Pb compositions, different from those in the host basalts, but very close to those a Piñón basalt sampled in Guayaquil area. Homogeneous Nd isotopic ratios are consistent with derivation of the three felsic rocks from a common source, but very limited, small-scale variability in Sr and Pb isotopic composition suggests additional crustal assimilation and/or hydrothermal alteration.

8. Discussion

8.1 Spatial, temporal and geochemical relationships between Pascuales felsic rocks and Las Orquideas volcanic rocks

Both the Pascuales and LO magmatic rocks crop out in the same region of the CCH west of Guayaquil. On one hand, Pascuales tonalites and trondhjemites are intrusive within basalts that are similar to oceanic plateau basalts of the Piñón Fm. forming the basement of the CCH (Fig. 3) in terms of major elements, trace elements, and isotopes. On the other hand, LO dacites were sampled in Rio La Derecha and Rio Guaraguau located 30-40 km west from Pascuales, where they conformably overlay the top of the Piñón basalts (van Melle et al.,

2008). The LO volcanic rocks are interbedded with limestones that contain pelagic microfauna indicating a Coniacian age (Ordoñez, 2007; van Melle et al., 2008; Velasco and Mendoza, 2003), i.e. corresponding to an age of ~88 Ma according to the time scale of Gradstein et al. (2004). This age is consistent with the radiometric ages of 87–89 Ma obtained here and interpreted as the time of crystallization of the plutonic felsic rocks, indicating that the plutonic and volcanic events were coeval, or at least penecontemporaneous.

In addition to be closely spatially and temporally related both rock types share peculiar geochemical characteristics that clearly distinguish them from Cretaceous Ecuadorian arc-related volcanic rocks. Indeed, despite some scatter in K_2O , Ba, Sr (due to the mobility of these elements during alteration) and in Al_2O_3 , Na_2O and MgO (ascribed to variable abundances of plagioclase \pm pyroxene phenocrysts in the LO volcanic rocks, van Melle et al., 2008; Reynaud et al., 1999), Harker diagrams (Figs. 7 and 8) and plots of REE, Th, Zr and Y versus Nb (Fig. S2) show that the two Pascuales tonalites and the four LO dacites (~63–70 wt.% SiO_2) plot in the same compositional fields. The trondhjemitic samples extend these fields toward high-silica rhyolitic compositions despite the gap between ~70 and ~78 wt.% SiO_2 . All these rocks share the same low concentrations in incompatible minor elements (Ti, K, P) and extreme depletions in REE and Y (excepted one LO dacite enriched in K), that distinguish them from the Rio Cala Arc dacites. Very low K_2O , TiO_2 , HREE and Y concentrations also characterize the Pujilí Granite, but the latter is characterized by much higher La (40.2 ppm versus 3.7–5.0 ppm in Pascuales tonalites) and lower Yb (0.2 ppm versus 0.7 ppm in Pascuales tonalites) concentrations, yielding strongly fractionated normalized REE patterns ($La/Yb_{CN} = 32$ in Pujili Granite versus 3.6–4.7 in Pascuales tonalites; Fig. 9A) indicative of residual garnet in the source of the Pujili Granite (Vallejo, 2007) but not in that of the Pascuales tonalites. As a whole, major element compositions of Pascuales and LO felsic rocks form linear trends of decreasing MgO , Fe_2O_3 , CaO , Al_2O_3 ,

P_2O_5 and Sr, and increasing Na_2O , La, Nb, Th and Zr with increasing SiO_2 (Figs 7 and 8). Excluding the two LO andesitic/dacitic samples more enriched in MgO, the Pascuales felsic rocks and the three LO MgO-poor dacites these trends appear to be consistent with fractional crystallization of plagioclase, amphibole \pm pyroxene and apatite, as generally observed in the latest stages of differentiation of calc-alkaline magmatic series. From the tonalites to the trondhjemites, La/Yb_{CN} values slightly increase from 3.6–4.7 to 4.4–6.5. The latter also have lower concentrations in Y, HREE and MREE (Y and Sm vs. SiO_2 in Fig. 8), with concomitant decrease in (Sm/Yb)_{PM} from 2.4 in the tonalites to 1.6 in the trondhjemites, whereas (Zr/Sm)_{PM} increase from 1.3–1.5 in the tonalites to 2.2–3.8 in the trondhjemites. These features are interpreted as reflecting an increased control of the amphibole on the silica-rich liquid during magmatic differentiation (e.g., Davidson et al., 2007; Brophy, 2008; Dessimoz et al., 2012; Nandedkar et al., 2016; see section 8.2 for more details). The sample GD002 has the highest silica content and exhibits the strongest amphibole signature (Fig. 9B, C). This sample also displays a positive Eu anomaly, whereas the other two samples show no Eu anomalies. A positive Eu anomaly is generally thought to reflect plagioclase accumulation, but enrichment/depletion of Eu with respect to adjacent REE also result from competition between amphibole and plagioclase during fractionation (Tarney et al., 1979; Dessimoz et al., 2012) as suggested by higher Sr/Y ratios in the tonalites (Sr/Y = 31–32) with respect to the trondhjemites (Sr/Y = 9–16).

Cogenetic relationships are supported for the tonalites and trondhjemites which share similar $^{143}Nd/^{144}Nd$ ratios. However, the two LO MgO-rich samples (EQ94.1 and EQ94.2) analyzed by Reynaud et al. (1999) cannot have the same source composition as the Pascuales felsic rocks because they exhibit ϵNd_i values (+6.02 and +7.14, respectively) significantly higher than those of Pascuales tonalites and trondhjemites (+4.41 to +5.59). These two LO lavas contain Mg-rich pyroxene phenocrysts (Reynaud et al., 1999) and could be explained by

566 mixing between a felsic melt and a mafic (liquid or solid) component, as suggested by the
567 decrease of the ϵNd_i values with increasing SiO_2 and Nb contents (Fig. 11) and the linear
568 compositional trend in the MgO-SiO_2 binary diagram (Fig. 7). No isotopic data are available
569 for the other LO dacites and they are not directly associated on the field, therefore, they might
570 not be genetically related to Pascuales felsic rocks and might also plot on the same mixing
571 trends. Nevertheless, because both rock types share the same geochemical features and
572 display subparallel, similarly fractionated trace element patterns (Fig. 9), it is assumed that a
573 derivation from magmas having close compositions and/or that evolved via similar magmatic
574 processes took place.

575 Our new geochemical and chronological data together with previous regional
576 models allow to propose that: (i) the Pascuales tonalites can be considered as plutonic
577 equivalents of the LO dacites, representing a same magmatic episode; (ii) this magmatic
578 episode is middle-Coniacian, based on zircon dating of Pascuales intrusives, in agreement
579 with microfauna contained in LO sediments; (iii) the LO volcanites rest directly on the top of
580 the Piñón basalts, yielding a minimum late Turonian – early Coniacian age (~88–90 Ma) for
581 the basaltic exposure in this area (Luzieux et al., 2006; Ordoñez et al., 2006; van Melle et al.,
582 2008). LO volcanites and associated sediments are overlain by a thick pile of sediments of the
583 Calentura and Cayo Fms. dated, respectively, late-Coniacian to middle-Campanian, and
584 middle-late-Campanian (van Melle et al., 2008; Ordoñez et al., 2006). According to van Melle
585 et al. (2008) increasing abundance of volcanoclastic deposits and debris flows in the middle to
586 upper part of the Calentura Fm. suggests the onset of an instability period announcing the
587 construction of the San Lorenzo island arc. This arc was active from mid-Campanian to early-
588 middle Maastrichtian (~80–70 Ma) and was the source of the Cayo back-arc volcanoclastic
589 deposits. The short-lived Pascuales - LO magmatic episode exhibits atypical calc-alkaline
590 affinity and took place in the time interval (~90–80 Ma) that followed the final stage of

building of the oceanic plateau in coastal Ecuador and preceded self-sustained subduction zone beneath the San Lorenzo island arc. The possibility that this atypical magmatism was related to initiation of the Late Cretaceous subduction at the leading edge of the CLIP will be discussed section 8.3.2. Interestingly, the LO Member is intruded by dolerites (samples 04LD01 and 04GW-01 analyzed by Allibon et al., 2008) that display major, trace element and lead and neodymium isotopic compositions within the range of the San Lorenzo and Rio Cala tholeiitic basalts and basaltic andesites (Figs. 7 and 8); according to Luzieux (2007) these intrusives would be coeval or younger than the Calentura Fm. and related to the San Lorenzo arc.

8.2 Geochemical constraints on the petrogenesis of Pascuales and Las Orquideas felsic rocks

Small bodies of tonalites and trondhjemites (also referred as oceanic plagiogranites, Coleman and Donato, 1979, see Koepke et al., 2007 for a review) and volcanic equivalents are relatively common in thickened oceanic crust in all types of oceanic settings (mid-oceanic ridges; back-arc spreading centers; plume-related plateau basalts; subduction zones) and in ophiolites. Based on inferences from field relationships, trace element geochemistry and isotope compositions, they are believed to represent products of either differentiated basaltic magmas (e.g., Lippard et al., 1986; Amri et al., 1996; Floyd et al., 1998; Selbekk et al., 1998; Rao et al., 2004; Bonev and Stampfli, 2009; Rollinson, 2009; Haase et al., 2016), or partial melting of hydrated basalts, gabbros or sheeted dikes (e.g., Gerlach et al., 1981; Pedersen and Malpas, 1984; Flagler and Spray, 1991; Floyd et al., 1998; Selbekk et al., 1998; Gillis and Coogan, 2002; Koepke et al., 2007; Brophy, 2009; Rollinson, 2009; Brophy and Pu, 2012;

Tsuchiya et al., 2013; France et al., 2014), or both fractional crystallization and partial melting of hydrated mafic rocks (Wanless et al., 2010).

Pascuales tonalites and LO dacites overlap in terms of most major elements with calc-alkaline, silica-rich (63–75 wt.% SiO₂) experimental melts produced by crystal differentiation of hydrated tholeiitic basaltic and andesitic magmas, as well as those produced by dehydration melting of amphibolite and hydrous partial melting of basalt and gabbro, under varying conditions of pressure, water content and oxygen fugacity (e.g., Dixon-Spulber and Rutherford, 1983; Koepke et al., 2004; Berndt et al., 2005; Sisson et Kelemen, 2005; France et al., 2010, 2014; Blatter et al., 2013; Nandedkar et al., 2014; Müntener and Ulmer, 2018, among other; Fig. S3). Considering FeO*/MgO ratios and incompatible minor elements; the Fig. 12 shows that Pascuales tonalites and LO dacites have the lowest FeO*/MgO ratios and K₂O, TiO₂, P₂O₅ concentrations at given SiO₂ and MgO contents. Such low FeO*/MgO ratios and extreme depletion in TiO₂ in dacitic compositions exclude an origin by fractional crystallization of anhydrous tholeiites (e.g., Dixon-Spulber and Rutherford, 1983; Berndt et al., 2005), and thus an origin of Pascuales tonalites and LO dacites by differentiation of Piñón basaltic magmas. Instead they argue for a magmatic evolution under high water contents and/or high oxidizing conditions. Low to very low K, Ti and P concentrations in experimental dacites and rhyodacites and natural plutonic equivalents have been interpreted mainly as reflecting depletions in the parent basalt (Dixon-Spulber and Rutherford, 1983; Beard and Lofgren, 1991; Koepke et al., 2004; Berndt et al., 2005). Alternatively, water-saturated partial melting of mafic rocks yields silicic melts with low FeO*/MgO and TiO₂ contents explained by crystallization of Fe-Ti oxides (Beard and Lofgren, 1991), whereas low P₂O₅ contents may reflect the presence of residual apatite in the solid residues (Wanless et al., 2010). For Koepke et al. (2004, 2007), extreme depletion in TiO₂ contents in intermediate and silicic partial melts reflects a refractory protolith and is a key parameter to discriminate between plagiogranite

generated by anatexis of hydrothermally altered cumulate gabbro from plagiogranite formed by differentiation of basaltic magmas in the oceanic crust.

The anomalously low REE contents of the Pascuales tonalites and LO dacites with respect to common calc-alkaline silicic rocks imply additional constraints. Amphibole is an important hydrous phase that accommodates higher amounts of REE and other highly incompatible elements than other major anhydrous phases (i.e., olivine, pyroxenes, plagioclase) during the evolution of water-rich magmas. Because its stability increases with increasing amount of water in the magma and with increasing pressure (Grove et al., 2003; Barclay and Carmichael, 2004), its crystallization in water-rich, arc magmas in the lower crust has for effects to dramatically reduce the REE increase rate and significantly modify incompatible trace element ratios in the derivative melts (Davidson et al., 2007; Rodriguez et al., 2007; Brophy, 2008; Rollinson, 2009; France et al., 2014; Nandedkar et al., 2016). Similarly, amphibole, either as a residual phase (dehydration melting of amphibolite) or as a reacting phase (hydrous partial melting), exerts a control over the REE in the low-degree, silica-rich, partial melts from mafic rocks, because their incompatibility continuously decreases with increasing liquid SiO₂ contents, eventually shifting from incompatible to compatible (e.g., Sisson, 1994; Klein et al., 1997; Dalpe and Baker, 2000; Nandedkar et al., 2016). Experimentally-based numerical models have explored the REE behaviors, absolute abundances and degrees of enrichment (or enrichment factor F) in felsic magmas (~63–76 wt.% SiO₂) relative to the initial rock source or parent basalt for various compositions and different depths and mechanisms of differentiation. They show that REE concentrations in residual liquids slowly increase (F ~1.2–1.4, Brophy, 2008) or remain nearly constant (F ~0.5, Rodriguez et al., 2007; F ~0.9, Nandedkar et al., 2016) over the entire range of differentiation of arc magmas if amphibole is a major early fractionating phase at lower crustal pressures (\geq 0.7 GPa, Alonzo-Perez et al., 2008; Blatter et al., 2013; Ulmer et al., 2018). Assuming that

Pascuales and LO dacitic magmas were generated after removal of ~50% of an amphibole-rich assemblage from a water-rich arc magma, such low enrichment factors would require less than ~2.8–4.2 ppm of La and less than ~0.4–0.6 ppm of Yb in the parent basaltic magmas, well below the REE contents of the more primitive Rio Cala basalts (Fig. 8) and other common arc basalts, suggesting derivation from water-rich, highly depleted magmas. In partial melting scenarios, enrichment factors calculated by Brophy (2008) vary between 2.1 and 3.2 for La and between 0.4 and 2.3 for Yb in derivative partial melts for a similar 63–70 wt.% SiO₂ range, regardless the type (equilibrium, fractional, accumulated fractional) and mechanism (dehydration or hydration melting) of melting and compositions of the protolith. Application to Pascuales and LO dacitic rocks suggests strongly depleted rock sources containing 1.0–2.5 ppm of La and 0.3–1.8 ppm of Yb, more compatible with mafic–ultramafic cumulate protoliths rather than basaltic protoliths that solidified from slightly to moderately differentiated melts (see Fig. 12, France et al., 2014's experimental melting of MORB dykes).

Pascuales and LO felsics exhibit negative Nb anomalies in PM-normalized diagrams, a feature commonly attributed to an emplacement above a subduction zone. However, negative Nb anomalies is not always symptomatic of subduction settings as they are observed in Iceland and MOR dacites believed to be produced by low degrees of partial melting of hydrated oceanic crust (Gunnarsson et al., 1998; Haase et al., 2005; Wanless et al., 2010; Wilbold et al., 2009). Niobium is only moderately incompatible in amphibole equilibrated with silica-rich, calc-alkaline melts, with $D_{\text{Nb/La}}$ values above the unity, resulting in lower (Nb/La)_{PM} in the felsic melts (Foley et al., 2002; Haase et al., 2005; Münker et al., 2004). In addition, Nb concentrations in melt are also controlled by magnetite and ilmenite as stable phases in the restite. The extremely low REE concentrations observed in Pascuales felsic rocks and LO dacites also explain the Zr and Hf positive anomalies on the PM-normalized

multi-element patterns, which are not observed in common tonalites and dacites. Like the REE, HFSE become more compatible in amphibole with increasing silica contents in melts (e.g., Foley et al., 2002; Nandedkar et al., 2016), but REE compatibility increases faster than HFSE compatibilities, while MREE are preferentially incorporated over LREE and HREE. As a result, Zr/Sm ratios increase with increasing silica contents in H₂O-rich liquids (Davidson, 2007; Nandedkar et al., 2016; Wanless et al., 2010).

In conclusion, major and trace element data (i.e., low FeO*/MgO, very low Ti and REE contents, high Zr/Sm ratios) suggest that the formation of Pascuales and LO felsic rocks result from magmatic processes largely dominated by amphibole and Fe-Ti oxides, implying evolution at high water contents. This conclusion is also consistent with the explosive emplacement of the LO dacites (van Melle et al., 2008). These conditions can be fulfilled by two magmatic processes, hydrous partial melting of mafic-ultramafic material or high-pressure, fractional crystallization of water-rich, arc-related magmas (or by a combination of both processes). Both models require fluxing of hydrous fluids in the crustal protoliths or in the mantle sources. However, amphibole alone cannot explain the REE extreme depletion; unusually depleted compositions of the protoliths or parent magmas are also needed.

8.3 Geodynamic implications

8.3.1 The partial melting of mafic cumulates evidence

Several aspects support a model invoking partial melting of mafic cumulates to generate Pascuales dacitic magma(s): 1) The Pascuales plutonic bodies are intrusive within basalts that unambiguously belong to the Piñón OPB, and both formations are almost contemporaneous, which implies that the OPB were still hot during the emplacement of the plutons. If, in addition, water was provided, the temperature needed for generating dacitic

melts from a gabbroic protolith ($< 1000^{\circ}\text{C}$; e.g. Koepke et al., 2004, 2005) could have been reached. 2) Natural examples in modern tectonic settings, experimental work and modelling demonstrated that hydrous re-melting of mafic rocks yields K-poor calc-alkaline, rhyodacitic magmas characterized by arc-like features such as negative Nb anomalies, independently of the origin of the protolith (N- and E-MORB-types or island-arc tholeiites) and of the tectonic setting where partial melting took place (e.g. Haase et al., 2005; Wanless et al., 2010; Willbold et al., 2009). In addition, other features such as the positive Zr anomalies and low REE contents that distinguish the Pascuales felsics from common subduction-related dacites are also characteristics of hydrous partial melts from mafic rocks.

The isotopic data exclude a common source for the Pascuales basalts and felsics. However, a Piñón basalt sampled in the CCH (Ca1 in Fig. 10) exhibits a less radiogenic initial $^{143}\text{Nd}/^{144}\text{Nd}$ composition ($\epsilon\text{Nd}_i = +4.49$), slightly lower than those characterizing the tonalite and trondhjemitites, and plots below the fields of the CLIP and Galapagos Plume at 90 Ma (Fig. 10A, B). Although this composition is unique among the six basalts analyzed in the CCH (and among other Ecuadorian OPB), a few picrites and alkali basalts belonging to the ~90–89 Ma oceanic plateau in Tortugal (Costa Rica; Hauff et al., 2000a; Trela et al., 2017) and in the Beata Ridge (Caribbean Sea; Dürkefälden et al., 2019; Hauff et al., 2000a) have ϵNd_i values (down to +4.24 and +5.41, respectively) lower than those of the basalts from the Galapagos Plume. Indeed, the three Pascuales felsic rocks plot in a field defined by the Tortugal magmatic rocks in the initial ($^{143}\text{Nd}/^{144}\text{Nd}$) versus ($^{206}\text{Pb}/^{204}\text{Pb}$) diagram (Fig. 10B), suggesting that their protoliths could have derived from a mantle source region more enriched than those of the main CLIP magmatic rocks. This mantle source region would be a mixture of more radiogenic Nd and less radiogenic Pb isotopic compositions than common CLIP rocks, and less radiogenic Nd and more radiogenic Pb isotopic compositions such as those characterizing the Tortugal picrites and alkali basalts.

In the Ecuadorian Western Cordillera, early to late Cretaceous ultramafic and mafic rocks believed to represent lower crust fragments of the Pallantaga oceanic plateau such as the San Juan cumulates (Hughes and Pilatasig, 2002; Jaillard et al., 2009; Lapierre et al., 2000; Mamberti et al., 2004) and the Tortoras mafic granulites and amphibolites (Amortegui et al., 2011; Beaudon et al., 2005) (Fig. 2) also have the low REE and Ti compositions required to represent the protoliths of the Pascuales felsic magma. Nd-Sr-Pb isotopic data for these two terranes are shown in Fig. S4. The San Juan Unit exposes peridotites, layered werhlites, and layered and isotropic gabbros that yield a Sm/Nd isochron of 123 ± 13 Ma (Lapierre et al. 2000) and a zircon U/Pb age of 87.1 ± 1.6 Ma (Vallejo et al., 2006) and shows variable geochemical and isotopic compositions (Mamberti et al., 2004; Fig. S4A), indicating intercalation of two distinct magmatic sequences, possibly representing intrusions of a younger, Late Cretaceous, oceanic plateau magmas in an older, Early Cretaceous, oceanic plateau (Jaillard et al., 2009; Mamberti et al., 2004; Spikings et al., 2015; Vallejo et al., 2009). Values of ϵNd_i in San Juan cumulates range from +8.1 to +2.5 overlapping those of the Piñón OPB and Pascuales mafic and felsic rocks, but their $(^{206}\text{Pb}/^{204}\text{Pb})_i$ ratios are significantly lower (< 18.5 ; overlapping the picrites from the Guaranda terrane of the Pallatanga Unit; Mambeti et al., 2003), which precludes involvement of cumulates with similar isotopic compositions as protoliths of the Pascuales dacitic magma. The Tortoras granulite and amphibolites also span a wide range of $(^{143}\text{Nd}/^{144}\text{Nd})_i$ (ϵNd_i values ranging from +7.9 to +1.8) but display more radiogenic Sr and Pb isotopic compositions. The range of $(^{206}\text{Pb}/^{204}\text{Pb})_i$ (18.72–19.07) is quite restricted and, in the initial $(^{143}\text{Nd}/^{144}\text{Nd})$ versus $(^{206}\text{Pb}/^{204}\text{Pb})$ diagram (Fig. S4B), their compositions overlap with those of Pascuales rocks. The amphibolites that have the lowest $(^{143}\text{Nd}/^{144}\text{Nd})_i$ ratios are those that have the highest $(^{207}\text{Pb}/^{204}\text{Pb})_i$ ratios (Fig. S4C) and $(^{208}\text{Pb}/^{204}\text{Pb})_i$ (not shown), which is consistent with mixing with pelagic sediment. Such enrichments in radiogenic Pb likely occurred during the deformation and amphibolitisation of

the former basalts and cumulates. In contrast, isotopic compositions of the amphibolites the least enriched in radiogenic Pb plot with the Pascuales felsic rocks in the Nd–Pb isotopic spaces overlapping, or not far from, the OPB, Tortugal and Galapagos fields (Figs. S4 B, C), indicating restricted or no contribution of sediment. Chemical and isotopic compositions of Tortoras metamorphic cumulates thus compared well with the compositions expected for the protoliths of Pascuales dacitic magma. However, low radiogenic Nd composition of the trondhjemite CP603 is not correlated with higher values of $(^{207}\text{Pb}/^{204}\text{Pb})_i$ and $(^{208}\text{Pb}/^{204}\text{Pb})_i$ ratios, suggesting that its lower $(^{143}\text{Nd}/^{144}\text{Nd})_i$ ratio may be a primary feature of the mantle source region. The slight enrichments in radiogenic Pb observed in the samples GD001 and GD003 with respect to CP603 indicate very small-scale variations likely reflecting post-magmatic contamination.

High temperature metamorphism and granulite formation are commonly associated with partial melting of the protolith. The metamorphism of the Tortoras rocks was dated around 85 Ma in hornblende, a cooling age that post-dated the peak metamorphism (Vallejo et al., 2006, 2009), which is also the age of the Pujili Granite (Vallejo et al., 2009). The granulite and amphibolites experienced peak metamorphic conditions of 800°–850°C in the plagioclase stability field (<6–9 kbar; Beaudon et al., 2005) and they include metamorphic mantle peridotite in addition to metacumulate (Amortegui et al., 2011), therefore regional metamorphism likely occurred at the crust – lithospheric mantle boundary, at the base of a 20–25 km thick oceanic crust consistent with the estimate thickness for the Caribbean plateau crust (Mauffret and Leroy, 1997). It is reasonable to believe that similar lithologies undergoing similar processes were also present at the base of the Piñón Fm. in the CCH, providing possible sources for the Pascuales and LO felsic magmas (see also the deep crustal xenolith suites in SW Colombia for similar lithologies, Weber et al., 2002). Further evidence may be represented by the Piñón amphibole-bearing gabbros that yielded a cooling age of ca.

89 Ma (Luzieux et al., 2006) and which are now exposed ~20 km north of the Pascuales area. Indeed, the crystallization history of this gabbro may have coincided with melting of Piñón cumulates, and thus with the generation of the Pascuales and LO felsic magmas. Unfortunately, no detailed petrographic and geochemical data were published for these hornblende-bearing gabbros, so they may be interpreted as either a residual material of partial melting or as cumulates of arc magma differentiation, both types being almost petrographically indistinguishable (Ulmer et al., 2018).

In summary, major, trace and isotopic compositions are compatible with an origin of the Pascuales felsics by partial melting of mafic cumulates assumed to be present in the lower crust of the Piñón Fm. and possibly belonging to an older plume-related magmatic pulse or event. The protoliths might have derived from a mantle source region characterized by lower radiogenic Nd and more radiogenic Pb isotopic compositions than the common CLIP rocks. Alternatively, the low Nd radiogenic signature could result from addition of a small amount of pelagic sediments. It is assumed then that partial melting must have occurred in a hot and dynamic environment associated with deformation, hydration and metamorphism of mafic-ultramafic protholiths in deep-seated shear zones.

8.3.2 Felsic intrusions: a subduction initiation signature?

In several places in the Northwestern Andes and the Caribbean, the CLIP is intruded by gabbroic plutons and tonalitic batholiths with arc-like affinity signature; these plutons emplaced soon after the OPB extrusion and most of them are interpreted as crystallization from juvenile, silicic magmas recording the initiation of an oceanic arc on the top of the oceanic plateau. These places include Western Colombia (e.g. Altamira, Zapata-Villada et al., 2017;

811 Buga, Villagomez et al., 2011; Bolivar Ultramafic Complex and Vijes (rhyodacitic) Felsites,
812 Kerr et al., 2004; Santa Fe and Burritica, Weber et al., 2015), Aruba (van de Lelij et al., 2010;
813 White et al, 1999; Wright and Wyld, 2011), Curaçao (Kerr et al., 1996 and Wright and Wyld,
814 2011); and Panama (Azüero Marginal Complex, Buchs et al, 2010). Some geochemical
815 similarities and differences between these felsic intrusions and the Pascuales and LO felsic
816 rocks are shown in Fig. S5. Compared to Pascuales tonalites, the Aruba, Santa Fe, Buritica
817 and Buga tonalites have higher overall REE abundances, but still lower than the Rio Cala
818 dacites, a difference that can be explained by refractory protholiths (gabbro cumulates) for
819 Pascuales and more enriched protoliths (basalts) for the other rocks. With the exception of the
820 Pujili Granite, all these rocks exhibit incompatible trace element contents and ratios indicating
821 that garnet had played no or very minor role as a residual phase, thus suggesting magma
822 generation at pressures lower than ~0.7 GPa. Like for LO volcanic rocks, these late
823 Cretaceous silicic intrusives have been interpreted as subduction-related based on calc-
824 alkaline affinities and Nb-Ta negative anomalies on N-MORB and PM-normalized multi-
825 element diagrams (see Whattam and Stern, 2015, for a review). However, as discussed in
826 Sections 8.2 and 8.3.1, partial melting of hydrated mafic rocks produces similar melt
827 compositions, and does not necessarily require plate subduction settings. In the other hand,
828 these intrusions occurred less than 10 Ma before steady-state, west-dipping subduction zones
829 beneath the San Lorenzo and Rio Cala intra-oceanic island arcs (see introductory section), a
830 time lag predicted by plate-tectonic models for the initiation of self-sustained subduction
831 zones (Stern and Gerya, 2018; Whattam and Stern, 2015). In this view, this silicic magmatism
832 that occurred shortly after (or even slightly overlap in time; van de Lelij et al., 2010; Whattam
833 and Stern, 2015) the eruption of the Piñón basalts can be interpreted as the earliest stage of
834 intra-oceanic subduction associated with widespread extension and asthenospheric upwelling

leading to the emplacement of basaltic magmas weakly or not affected by subduction fluids (Stern and Gerya, 2018).

On the basis of the lithologies and tectono-magmatic-metamorphic events recorded in Tortoras terrane, we propose that the hottest, deeper parts of the CCH oceanic plateau in Guayaquil area underwent similar high-temperature shear deformation and metamorphism and remelting triggered by intrusion and crystallization of younger mafic magmas in response to regional extension and asthenospheric upwelling. This agrees with crustal thickness estimates from forward modelling of potential data (Feinguer and Seguin, 1983; Aizprua et al., 2020) which define a ~7 km thick crust at the center-east CCH (i.e. 8 km thinner than unaffected plateau settings in west Ecuador). Without further evidence this thinning is tentatively ascribed to the same Late Cretaceous extensional episode. The composition of the upwelling mantle remains unknown since no basaltic lavas overly the top of the Piñón Fm. and the Ecuadorian OPB show no subduction contribution in their chemical signature (e.g. Hastie et al., 2013 and references therein). These underplating basalts could be either plume-related or hybrid between plume and arc as proposed by Whattam and Stern (2015) or arc basalts. A significant latent question is to know whether the Pascuales felsic rocks were co-magmatic or not with gabbroic and dioritic intrusions, as suggested by Pichler and Aly (1983) and Benitez (1995). Unfortunately, these rocks have not been clearly identified in the area and therefore, they have never been studied, nor dated. The lack of ~87–89 Ma aged mafic plutons intruded into the plateau and clearly identified as subduction-related and the lack of bimodal volcanism in the LO Member make not possible to firmly assert that the Pascuales and LO silicic magmatism was related to initiation of the San Lorenzo arc. We cannot exclude local remelting of the oceanic plateau without subduction (i.e., gravitational instability, subsidence effects); examples of juvenile, K-poor, calc-alkaline, dacitic magmas are reported in the Iceland basaltic plateau (Wilbold et al., 2009). However, sedimentary recordings in the

Calentura Fm. (van Melle et al., 2008), the wealth of petrologic and geochronologic data and plate-tectonic models suggest that this region localized at the SW leading edge of the Caribbean plateau was subjected to tectonic instability during or just after the end of plume-related magmatism. Therefore, intrusions of new basaltic magmas during initiation of late Cretaceous subduction are presently the best explanation for the partial melting of the mafic rocks forming the Piñón Fm., as suggested for other tonalitic intrusions in the CLIP (e.g., Wright and Wyld, 2011; Weber et al., 2015).

9. Conclusions

1) Several 'granitic-like' igneous bodies intruded within basalts and metabasalts of the Piñón Fm. (OPB part of the Caribbean Large Igneous Province, CLIP) in SW Ecuador near the town of Pascuales. Petrographic and mineralogical analyses allow defining these intrusions as tonalites and trondhjemites. Zircon U-Pb ages obtained by LA-ICP-MS yield ca. ~87-89 Ma for one tonalite and two trondhjemites. Trace elements, field and chronological data indicate that they are related to Las Orquideas dacitic breccias, which emplaced on the Piñón Fm. during the Coniacian.

2) Geochemical compositions of the Pascuales felsic rocks are calc-alkaline but differ from typical subduction-generated magmatic rocks by lower FeO^*/MgO ratios, extreme depletions in TiO_2 and P_2O_5 , low La/Yb and moderately elevated Sr/Y ratios. In addition, on primitive mantle-normalized multi-element diagrams, they are only moderately depleted in Nb relative to La and enriched in Zr relative to Sm. Similar compositions are reproduced by experiments and modeling of hydrous partial melting of mafic protoliths, and observed as intrusions in oceanic crust in orogenic and anorogenic tectonic settings. However Pascuales

felsic rocks are characterized by extreme depletions in REE and Y, which are not observed in other felsic intrusives of similar ages emplaced in the CLIP.

3) Isotope systematics (Nd-Sr-Pb) are robust for Nd and only marginally affected by alteration for Sr and Pb data for the felsic bodies. Their isotope compositions overlap with the field of the Caribbean oceanic plateau basalts, but plot at the least radiogenic Nd end-member compositions.

4) The wealth of geochemical and isotopical data are consistent with partial melting of hydrated OPB and can be accounted by a strong control of residual amphibole and Fe-Ti oxides during the formation of the magmas. In addition, geochemical modeling and nature analogues show that the extreme REE and Y concentrations require hydrous partial melting of refractory mafic cumulates rather than less depleted basaltic protoliths.

5) The geochemical, chronological and geodynamic context suggest that both the Pascuales and Las Orquideas felsic rocks represent silicic magmatism resulting from partial melting of the deeper crust of the oceanic plateau during the final stage of its building. The occurrence of this magmatism at the SW border of the CLIP, less than 10 Ma before the activity of the subduction zones beneath the San Lorenzo - Rio Cala intra-oceanic island arcs, suggests that the melting event may be related to the initiation of the subduction during Late Cretaceous.

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Figure Captions

Fig. 1. (A) Plume-induced subduction initiation model of the Caribbean Large Igneous Province (CLIP) between 89-85 Ma (modified from Whattam and Stern, 2014). Green areas show supposed active arcs. (B) Geodynamic cartoon showing the configuration of central-south Ecuador and north Peru. Abbreviations are as follows: AM, Amotapes massif; CCH, Chongón-Colonche hills; JF, Jubones fault; NAP, North American plate; SAP, South American plate; WC, Western Cordillera.

1498 Fig. 2. (A) Geological map of the Western Cordillera and forearc areas of Ecuador (Eguez et
1499 al., 2017). (B) Simplified geologic columns representative of western Ecuador. Abbreviations
1500 are as follows: CCH, Chongón-Colonche Hills; MB, Manabí basin; PB, Progreso basin; PG,
1501 Pujilí Granite; TA, Tortoras amphibolite; SJ, San Juan Unit; POPB, Pinon oceanic plateau
1502 basal; WC, Western Cordillera.

1503

1504 Fig. 3. (A) Aerial view of the Pascuales area (Google Earth image) showing sample location
1505 and the intrusive bodies (red polygons). (B, C) Field photographs of tonalitic and
1506 trondhjemitic outcrops. (D) Field photography of the basalt GD004. The asterisk refers to
1507 dated samples.

1508

1509 Fig. 4. Composition of clinopyroxenes and amphiboles from the studied Pascuales rocks. (A)
1510 Pyroxenes from the metabasalts CP605 and GD004 in the Mg-Ca-Fe diagram of Morimoto et
1511 al. (1998). (B) Variation of Al_2O_3 (wt. %) vs. Mg# in CP605 and GD004 clinopyroxenes. (C)
1512 Variation of Mg# vs. Si in amphiboles from the tonalite CP601 and the metabasalts CP605
1513 and CP607. (D) Variations of $(\text{Na} + \text{K})_{\text{A}}$ vs. Al^{IV} in amphiboles from the tonalite CP601 and
1514 the metabasalts CP605 and CP607. In panels (C) and (D), relicts of aluminous amphiboles
1515 preserved in late-stage magnesio-hornblendes are circled. Numbers of atoms per formula
1516 unit (apfu) in amphiboles are calculated on the basis of 13 cations excluding Ca, Na, K.
1517 Nomenclature of amphiboles from Leake et al. (1997). Sample locations are shown on Fig. 3.

1518

1519 Fig. 5. (A) Terra Wasserburg diagram for the tonalite CP024. (B) Terra Wasserburg diagram
1520 for the tonalite CP601. (C) Terra Wasserburg diagram for the trondhjemitic CP603.

1521

1522 Fig. 6. Normative Ab-An-Or plots of the Pascuales felsic plutonic rocks (this study) along
1523 with Las Orquideas volcanic rocks (data from Reynaud et al., 1999 and van Melle et al.,
1524 2008). Fields are after Baker (1979): tonalites (To), trondhjemites (Tr), granodiorites (Gd)
1525 and granites (Gr).

1526

1527 Fig.7. Harker diagrams showing major oxide variations against SiO₂ (wt.%) of the studied
1528 Pascuales basaltic lavas and felsic plutonic rocks. Other late Cretaceous Ecuadorian magmatic
1529 rocks are projected for comparison with the studied rocks; data are from: (1) Reynaud et al.
1530 (1999), Kerr et al. (2002a), Mamberti et al. (2003), Vallejo (2007), Chiarada (2009), and
1531 Allibon et al. (2008) for Ecuadorian oceanic plateau basalts (OPB); Piñón basalts collected in
1532 the Chongón-Colonche Hills (CCH) have been distinguished by a black spot. (2) Reynaud et
1533 al. (1999) and van Melle et al. (2008) for Las Orquideas (LO) volcanic rocks, and from
1534 Allibon et al. (2008) for the dolerites. (3) Cosma et al. (1998), Reynaud et al. (1999), Kerr et
1535 al. (2002a), Vallejo (2007), Allibon et al. (2008), and Chiarada (2009), for island arc volcanic
1536 rocks of the San Lorenzo Fm. and Rio Cala Arc. (4) Vallejo (2007) for the Pujili Granite.

1537

1538 Fig. 8. Variations of selected incompatible trace element contents (ppm) against SiO₂ (wt.%)
1539 for the studied Pascuales basaltic lavas and felsic plutonic rocks. Data sources for other Late
1540 Cretaceous Ecuador magmatic rocks same as Fig. 7.

1541

Fig. 9. (A) Chondrite-normalized REE patterns of Pascuales tonalitic samples. (B) Chondrite-normalized REE patterns of Pascuales trondhjemitic samples. (C) Multi-element patterns normalized to primitive mantle (PM) of Pascuales tonalitic and trondhjemitic samples. (D) Chondrite-normalized REE patterns of Pascuales basaltic samples. (E) Multi-element patterns normalized to N-MORB of Pascuales basaltic samples. In panels A–C gray field is for Rio Cala Arc volcanic rocks with $\text{SiO}_2 \geq 56$ wt.%. In panel D gray field is for other Ecuador oceanic plateau basalts and dolerites. Data sources for Las Orquideas, Rio Cala Arc and oceanic plateau magmatic rocks same as Fig. 7. Normalizing values are from Sun and McDonough (1989).

Fig. 10. Initial Nd, Sr and Pb isotope plots of the studied Pascuales basaltic lavas and felsic plutonic rocks. Data for Ecuadorian OPB and Piñón (CCH) basalts and dolerites are from Reynaud et al. (1999), Mamberti et al. (2003), Vallejo (2007) and Lapierre et al. (2000). Data for Rio Cala Arc and San Lorenzo Fm. volcanic rocks are from Cosma et al. (1998), Reynaud et al. (1999), Vallejo (2007), Allibon et al. (2008) and Chiarada (2009). In (A) the two Las Orquideas (LO) samples are the MgO-rich, silica-rich volcanic rocks (Reynaud et al., 1999); no isotope data have been published for the LO Mg-poor dacitic samples; in (B–D) data for LO dolerites are from Allibon et al. (2008). Are also reported Tortugal picrites and alkali basalts from Hauff et al. (2000a) and Trela et al. (2017). The fields of the Galapagos Plume, Pacific N-MORB and pelagic sediments at 90 Ma are from Hauff et al. (2000a,b) and the field of the Caribbean Large Igneous Province (CLIP) is after Kerr et al. (1996, 1997). The global composition of subducting sediment (GLOSS) is Plank and Langmuir (1998), the Northern Hemisphere Reference Line (NHRL) is from Hart (1984) and the Bulk Silicate Earth (BSE) is from Zindler and Hart (1986).

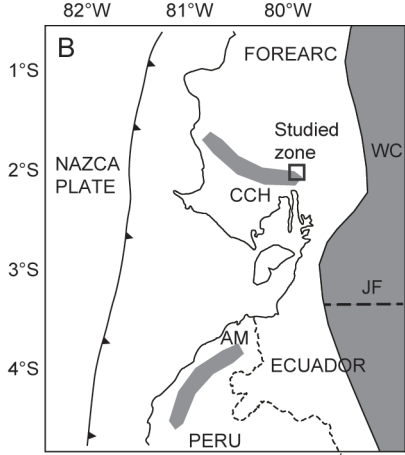
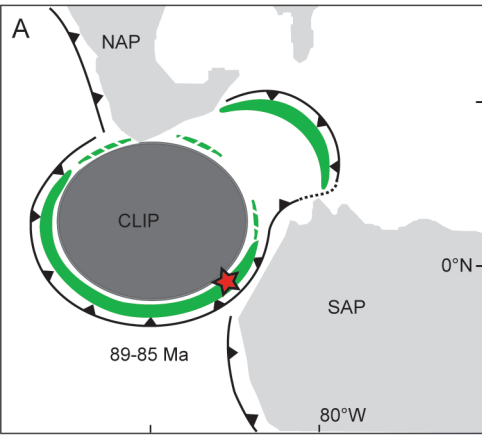
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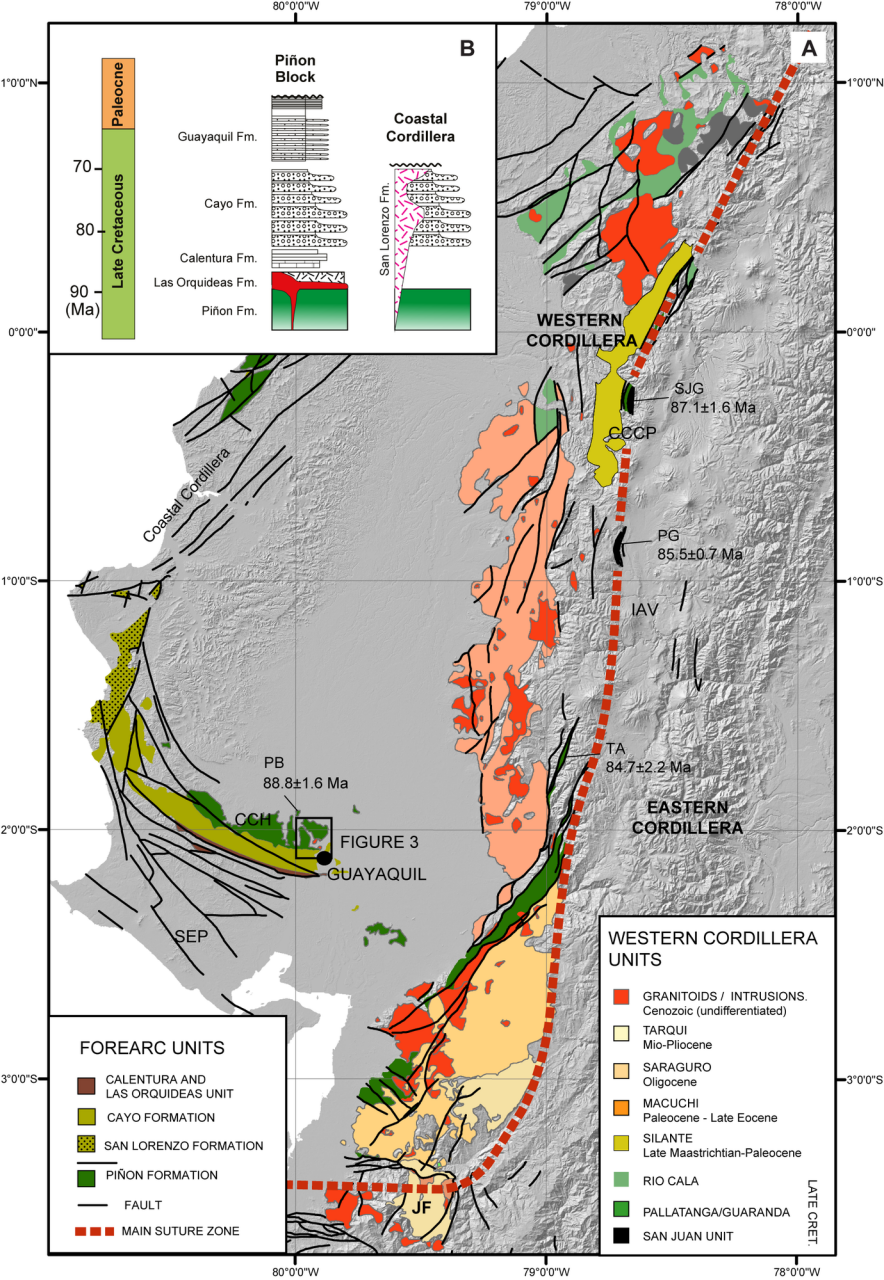
1567 Fig. 11. Variations of initial radiogenic Nd isotope vs. SiO₂ (wt. %) and Nb (ppm) for the
1568 Pascuales basaltic lavas and felsic plutonic rocks and the two Las Orquideas (LO) MgO-rich,
1569 silicica-rich volcanic rocks rocks (data from Reynaud et al., 1999). No isotopic data are
1570 available for the LO MgO-poor dacites.

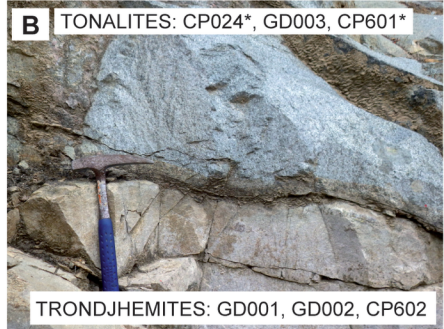
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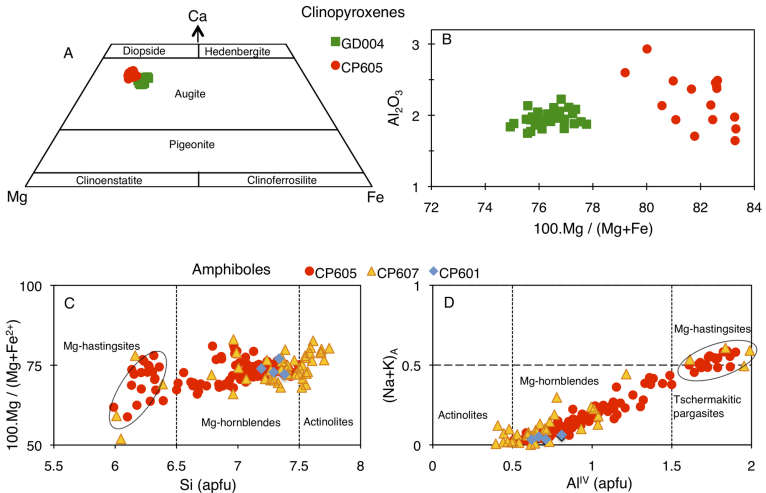
1572 Fig. 12. Comparison of Pascuales felsic (this study) and Las Orquideas (LO) dacitic
1573 compositions with melt compositions from experiments in Harker-type diagrams. (A) K₂O vs.
1574 SiO₂. (B) P₂O₅ vs. SiO₂. (C) FeO*/MgO vs. SiO₂. (D) TiO₂ vs. MgO. Experimental data for
1575 fractional crystallization (FC) of arc magmas at mid to lower crustal depths: Sisson et al.
1576 (2005), Blatter et al. (2013), Nandedkar et al. (2014), and Ulmer et al. (2018). Experimental
1577 data for hydrous partial melting (HPM) of rocks: Koepke et al. (2004) for hydrous partial
1578 melting of oceanic cumulate gabbros and France et al. (2010, 2014) for anatexis of
1579 hydrothermally altered mid-oceanic ridge sheeted dikes. Initial (in.) compositions of the
1580 gabbro protoliths (Koepke et al., 2004) are also shown. Tholeiitic (TH) and calc-alkaline (CA)
1581 fields are from Miyashiro (1974). High FeO*/MgO ratios of Pascuales trondhjemites are due
1582 to very low MgO contents.

1583









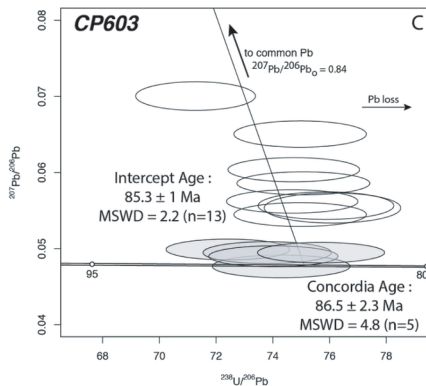
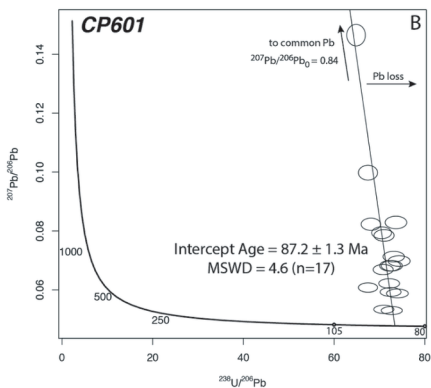
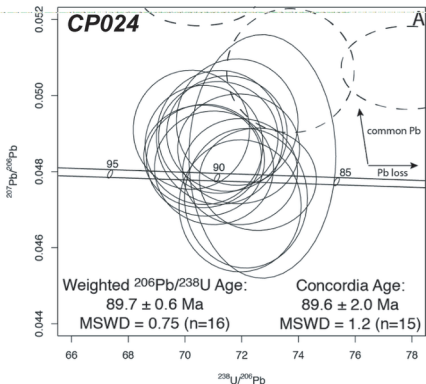
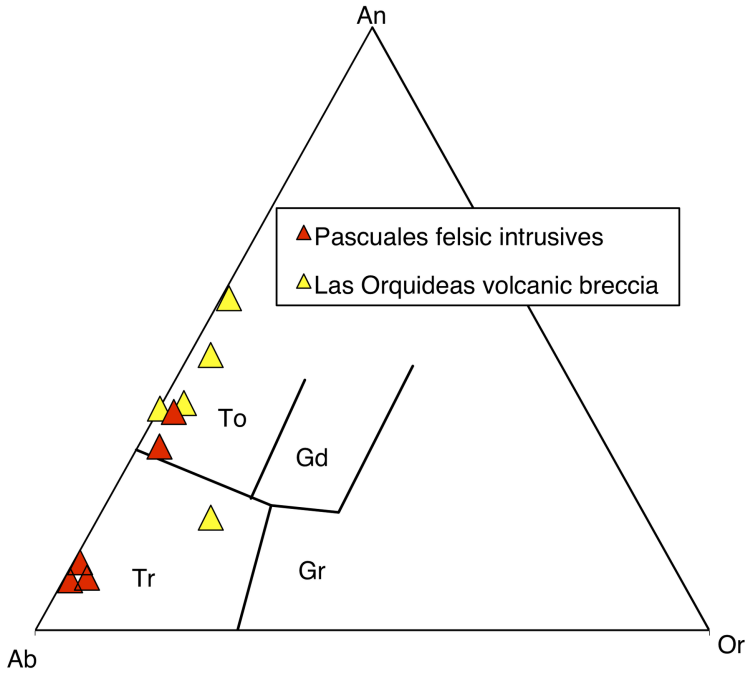
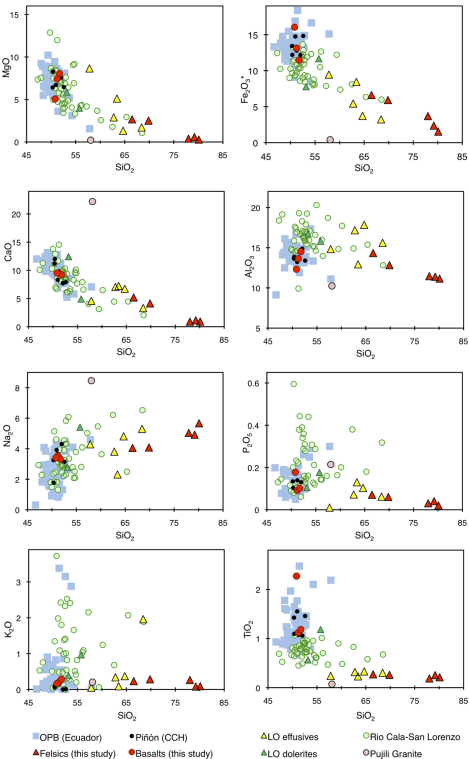
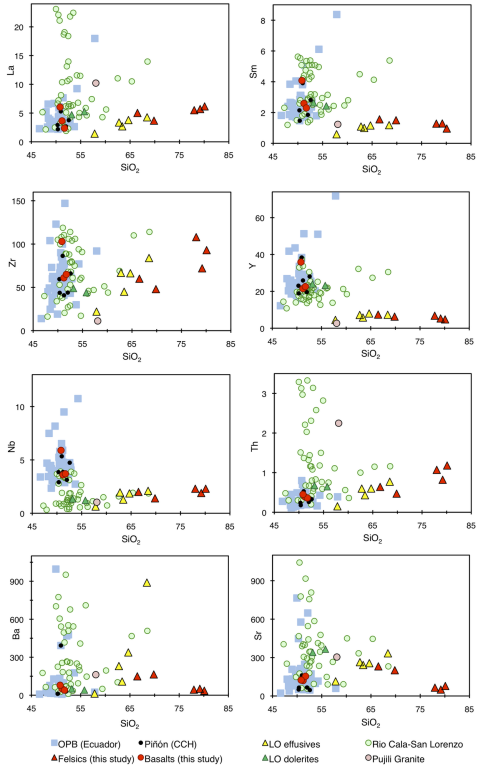
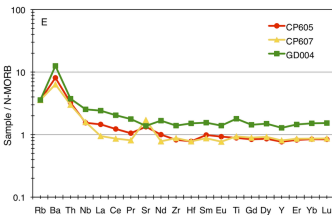
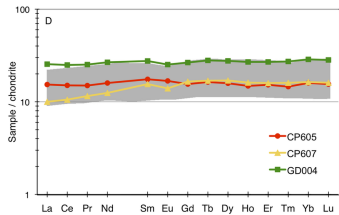
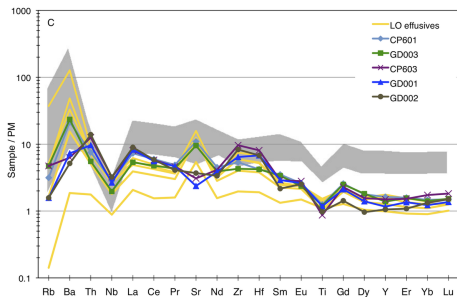
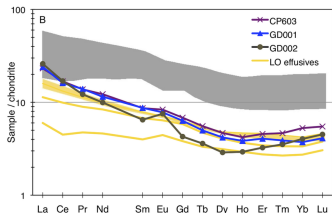
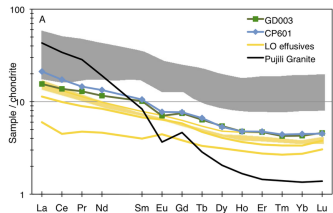


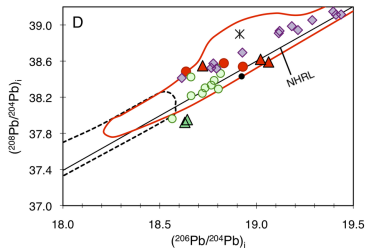
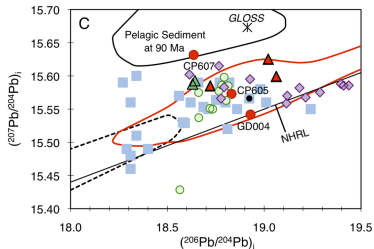
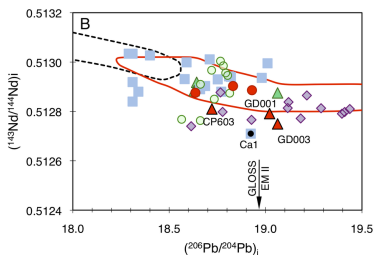
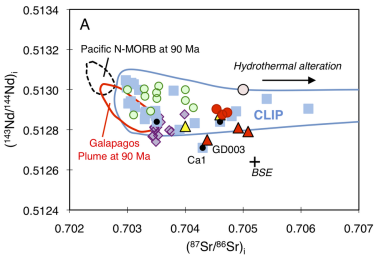
Figure 5. Seyler et al.











● Basalts (this study) ▲ Felsics (this study) ■ OPB (Ecuador)
 ● Piñón (CCH) ▲ LO effusives ○ Opujili Granite

○ Rio Cala-San Lorenzo ▲ LO dolerites ◆ Tortugal

