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Chlorine stable isotope variations across the Quaternary volcanic arc of Ecuador

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A B S T R A C T

Despite the potential of chlorine isotopes to trace inputs of fluids from the subducting slab, few studies so far have used this tool to investigate the petrogenesis of arc magmas. Here we report stable chlorine isotope data (δ^{37}Cl values) and Cl concentrations of volcanic rocks from five Quaternary volcanoes of Ecuador situated on an across-arc transect encompassing the frontal arc (Pilavo, Pululahua, Pichincha volcanoes), main arc (Chacana caldera complex) and back-arc (Sumaco volcano). We find that changes in δ^{37}Cl values across the arc correlate with slab fluid indices (Ba/La, Pb/Ce). The overall decrease in δ^{37}Cl values away from the trench can be interpreted in the frame of previous petrogenetic models of Ecuadorian volcanoes, according to which magmas are formed by a steadily decreasing melt fraction of the mantle induced by a steadily decreasing amount of fluids released by the subducted slab away from the trench. The high δ^{37}Cl values of the frontal arc volcanoes (up to +3‰) imply that the Cl carried by slab fluids derives, at least partly, from ^{37}Cl-rich subducted terrigenous sediments plus subordinate amounts of altered oceanic crust and serpentinite.

The anomalously high Cl contents (up to 0.2 wt.% Cl) and high δ^{37}Cl values (up to +1.5‰) of the back-arc Sumaco volcano can be explained by preferential partial melting of mantle portions metasomatized by slab fluids during a Jurassic subduction event.

Superimposed on the first order changes of δ^{37}Cl values across the arc, we observe that δ^{37}Cl values at each volcanic center are systematically lowered due to intracrustal evolution processes occurring in magmatic reservoirs at mid-crustal levels.

1. Introduction

Tracing the slab input in arc magmas is difficult because elements are released differentially from the subducting slab depending on the nature of the released fluid (i.e., aqueous fluid, silicic melt: e.g., Kessel et al., 2005) and the stability fields of H_2O-bearing mineral phases (e.g., Schmidt and Poli, 1998; Hacker et al., 2003). These depend on several factors, including depth along the slab and velocity of subduction, slab geometry and age, which influence the thermal structure of the subduction zone (e.g., Peacock and Wang, 1999; van Keken et al., 2002, 2011; Rüpke et al., 2004). The picture becomes even more complex when we try to deconvolute the slab signal in continental arcs, where the presence of a variably old and thick continental crust may perturb to a great extent the source signal of magmas through crustal assimilation.

Various radiogenic (Sr, Nd, Pb, Hf, Os) and stable light isotopes (O, B, Li, C), as well as elemental ratios (Ba/La, Pb/Ce, Th/La), have been used to trace and quantify the slab-derived component and its nature in arc magmas (e.g., Pearce, 1982; Hawkesworth et al., 1993; Elliott et al., 1997; Patino et al., 2000; Elliott, 2003; Shaw et al., 2003; Leeman et al., 2004; Eiler et al., 2005; Plank, 2005). Chlorine is an element with high solubility in aqueous fluids, as well as in silicic melts, although it will preferentially partition into a fluid over a melt (e.g., Carroll and Webster, 1994). Additionally, theoretical calculations predict limited chlorine stable isotope fractionation between fluid, melt, and silicates at high temperatures (Schauble et al., 2003). Chlorine cycling through crustal and mantle reservoirs depends on processes of alteration of the oceanic lithosphere, which increase their Cl concentration through sequestration of Cl in newly formed amphibole and serpentine minerals (e.g, Barnes and Sharp, 2006; Scambelluri et al., 2004; Kendrick et al., 2011; Philippot et al., 1998; Ito et al., 1983), and subduction of this lithosphere and overlying sediments into the mantle at convergent margins. Therefore, chlorine isotopes can be a useful addition to understand slab contributions in

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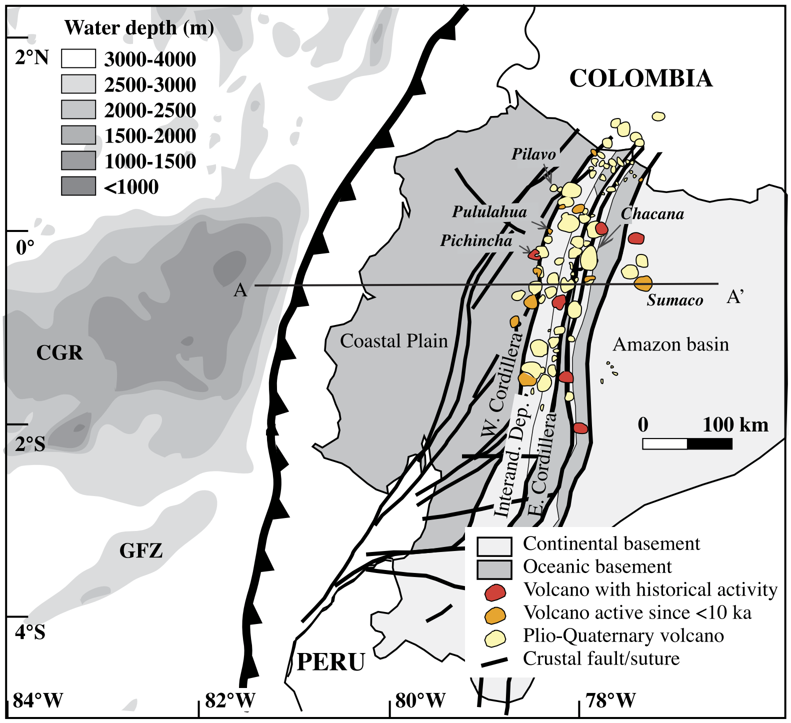

Fig. 1. Map of Ecuador with topographic features of the subducting plate (CGR = Carnegie ridge; GFZ = Grijalva fracture zone) and localization of recent and active volcanoes of Ecuador (modified after Litherland et al., 1994 and Corredor, 2003). Studied volcanoes are labeled with names. The A–A′ segment is the trace of the cross-section of Fig. 8.

subduction-related magmatic rocks, especially since the last years have seen a rapid development of analyses of magmatic rocks and a better definition of the isotopic compositions of mantle and crustal reservoirs (Sharp et al. 2007, 2013; Barnes and Sharp, 2006; Bonifacie et al., 2008a, 2008b; Layne et al., 2009; John et al., 2010, 2011; Barnes and Cisneros, 2012). Nonetheless, so far there are few published studies on stable chlorine isotopes in volcanic arcs (Barnes et al., 2008, 2009b; Barnes and Straub, 2010) and these are limited to the Central America and Izu–Bonin–Mariana subduction systems. Expanding the existing database of stable chlorine isotope compositions of arc magmas is necessary if we want to understand better the potential of chlorine isotopes as tracers of arc magma genesis.

Here, we present the first chlorine stable isotope data of Quaternary volcanic rocks of the Andes, in particular from the northern Andes of Ecuador. The Ecuadorian arc has been extensively studied in the past years, using a combination of geochemical tools (major and trace element geochemistry, stable and radiogenic isotopes, U-series) and mineral chemistry (e.g., Barragan et al., 1998; Bourdon et al., 2003; Chiaradia et al., 2004, 2009a, 2011, 2012, 2014; Le Voyer et al., 2008; Bryant et al., 2006; Garrison and Davidson, 2003; Garrison et al., 2006; Hidalgo et al., 2007; Hoffer et al., 2008; Samaniego et al., 2002, 2010; Schiano et al., 2010). The arc of Ecuador is characterized by the occurrence of three trench-parallel volcano chains stretching across-arc over a distance of >100 km (Fig. 1). Systematic geochemical changes across the three volcanic arc chains indicate a decreasing slab input from the frontal to the rear arc with attending decreasing partial melt amounts (Barragan et al., 1998; Le Voyer et al., 2008) producing subduction-related alkaline magmas in the back-arc (Sumaco, Pan de Azucar, Puyo volcanic centers).

Because of these systematic across-arc geochemical changes, the Ecuadorian arc is an ideal natural laboratory to evaluate the potential of stable chlorine isotopes as tracers of the decreasing slab signal from front to back-arc.

2. Geological setting

Ecuador consists of 5 physiographic domains (Fig. 1), which, from west to east, are: (i) Coastal Plain, (ii) Western Cordillera, (iii) Interandean depression, (iv) Eastern Cordillera, and (v) Amazon basin (Oriente). The Coastal Plain consists of the oceanic plateau terrane of Pallatanga, a fragment of the large Caribbean–Colombian Oceanic Plateau (CCOP) accreted to the continental margin during the Late Cretaceous (Kerr et al., 2002; Mamberti et al., 2003; Spikings et al., 2005; Vallejo et al., 2006, 2009). Gravimetric (Feininger and Seguin, 1983) and isotopic (Chiaradia and Fontboté, 2001; Chiaradia et al., 2008; Chiaradia, 2009) data indicate the occurrence of mafic crust of the Pallatanga terrane also at the base of the Western Cordillera of Ecuador (Fig. 1) (e.g., Kerr et al., 2002; Mamberti et al., 2003), overlain by Late Cretaceous to Tertiary arcs, formed both in allochthonous (i.e., pre-Late Cretaceous accretion: Rio Cala arc) and autochthonous positions (i.e., after the Late Cretaceous accretion: Macuchi and Silante arcs: Vallejo et al., 2009; Chiaradia, 2009). The estimated crustal thickness in the Western Cordillera ranges from 25–30 km (Feininger and Seguin, 1983) to 40–50 km (Guillier et al., 2001).

Less clear is the geology of the Interandean depression beneath the thick volcanic and volcaniclastic Tertiary to Quaternary sequences that conceal the basement. Litherland et al. (1994) suggest the occurrence of a continental terrane (Chaucha) in correspondence of the Interandean Depression.

The Eastern Cordillera consists of varied metamorphic lithologies including Jurassic metabasalts and Paleozoic schists and gneisses, that have been interpreted either as terranes of oceanic (Jurassic Alao island arc) and continental (Loja terrane) affinity accreted to the Amazon craton during the Late Jurassic–Early Cretaceous (Aspden and Litherland, 1992; Litherland et al., 1994; Noble et al., 1997) or as (para-)autochthonous sequences (Pratt et al., 2005; Cochrane et al., 2014). The crustal thickness in the Eastern Cordillera ranges from >50 km (Feininger and Seguin, 1983) to 50–75 km (Guillier et al., 2001).