



The role of crustal and eruptive processes versus source variations in controlling the oxidation state of iron in Central Andean magmas



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ABSTRACT

The composition of the continental crust is closely tied to subduction zone magmatism. Elevated oxygen fugacity (f_{O_2}) plays a central role in fostering crystallization of oxide minerals and thereby aids in generating the calc-alkaline trend of iron depletion that characterizes the continents. Along continental margins, arc magmas erupt through continental crust and often undergo extensive differentiation that may modify magmatic f_{O_2} . The importance of the subducting slab and mantle wedge relative to the effects of this differentiation on the f_{O_2} recorded by continental arc magmas remains relatively unconstrained. Here, we focus on the effect of differentiation on magmatic f_{O_2} using a suite of 14 samples from the Central Volcanic Zone (CVZ) of the Andes where the continental crust is atypically thick (60–80 km). The samples range in composition from ~55 to 74 wt% SiO₂ and represent the Neogene history of the arc. Samples are basaltic andesite to rhyolite and span a range of radiogenic isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr} = \sim 0.705\text{--}0.712$) that represent 30 to 100% crustal assimilation. We use several proxies to estimate the f_{O_2} recorded by lavas, pumice, and scoria: (1) whole rock $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, (2) $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in quartz-hosted melt inclusions, and (3) Fe–Ti oxide oxygen-barometry. Comparison of the f_{O_2} calculated from bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios (post-eruptive) with that derived from Fe–Ti oxides or melt inclusion $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios (pre-eruptive), enables us to quantify the effect of syn- or post-eruptive alteration, and to select rocks for bulk analysis appropriate for the determination of pre-eruptive magmatic f_{O_2} using a strict criterion developed here.

Across our sample suite, and in context with samples from the literature, we do not find evidence for systematic oxidation due to crystal fractionation or crustal contamination. Less evolved samples, ranging from 55 to 61 wt% SiO₂, record a range of >3 orders of magnitude in f_{O_2} , spanning the f_{O_2} range recorded by all samples in our suite. Among these less evolved magmas, we find that those erupted from volcanic centers located closer to the trench, closer to the Benioff Zone, and with more geochemical evidence of subducted components in the mantle source (elevated La/Nb) result in magmas that record systematically higher f_{O_2} . We conclude that the slab/mantle source can exert greater control on magmatic f_{O_2} than processes occurring in even the thickest continental crust. Thus, the f_{O_2} of arc magmas, and hence their calc-alkaline nature, may be inherited from the mantle.

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1. Introduction

The chemistry of arc magmas is intimately linked to the generation of continents (Gill, 1981). Oxygen fugacity (f_{O_2}) contributes to the creation of the calc-alkaline magmatic trends that typify arcs (e.g., Brounce et al., 2014; Kennedy, 1955; Osborn, 1959). Despite the observation that calc-alkaline magmas are generally

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more oxidized than tholeiites, no consensus exists on the oxidation mechanism. Degassing, fractional crystallization, and crustal contamination – all mechanisms of differentiation – have been suggested as possible vehicles for oxidation (e.g., Lee et al., 2005). Several studies have looked for magmatic oxidation due to degassing of C, H and S species in natural systems, but either have not observed it (Brounce et al., 2014; Cottrell and Kelley, 2011; Crabtree and Lange, 2012; de Moor et al., 2013; Kelley and Cottrell, 2012) or have discovered degassing-induced magmatic reduction (Anderson and Wright, 1972; Kelley and Cottrell, 2012; Moussallam et al., 2014; Shorttle et al., 2015). Low pressure fractional crystallization can result in moderate oxidation of less than

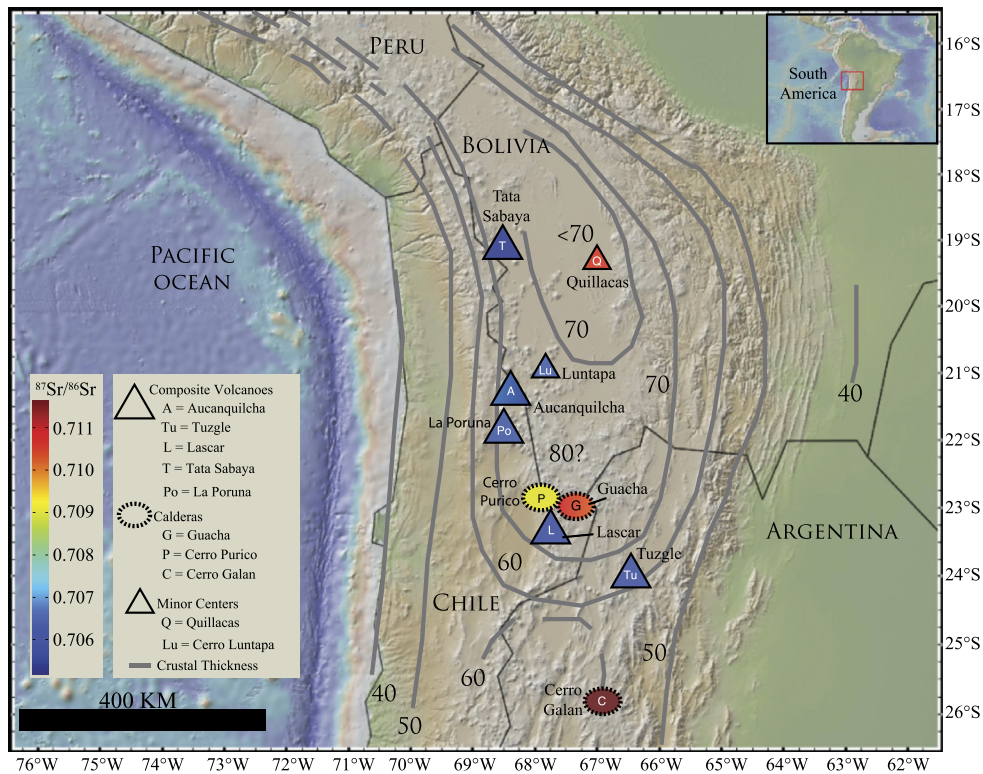


Fig. 1. The Central Volcanic Zone (CVZ) in the Andes of South America. Centers sampled span the entire CVZ and represent the complete range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as shown in the legend. Numbers refer to crustal thickness and are from Allmendinger et al. (1997). Base map from www.geomapp.org, Ryan et al. (2009).

half a log unit (Cottrell and Kelley, 2011) but cannot explain the disparity between the oxidation states of oceanic arc and mid-ocean ridge rocks (Brounce et al., 2014; Crabtree and Lange, 2012; Kelley and Cottrell, 2012). Crustal contamination (assimilation or partial melting of the host rock) can serve to reduce magmas (e.g., Hine et al., 1978), oxidize magmas (e.g., Ague and Brimhall, 1988), or produce no net change in oxidation state (e.g., Chappell and White, 2001), depending on the composition of the material being assimilated. The effects of crustal contamination on magmatic $f\text{O}_2$ are therefore not easily generalized and remain understudied. At continental arcs these processes have not been systematically evaluated and may operate to modify magmatic $f\text{O}_2$.

To investigate an end-member case, we examine the hypothesis that Central Andean magmas derive their oxidized nature from differentiation within an extremely thick continental crust. We focus on volcanic samples from the Central Volcanic Zone (CVZ) of the Andes in South America, where magmas have ascended through up to 80 km of continental crust (Fig. 1). CVZ volcanic rocks under consideration here have undergone variable amounts of differentiation as measured by their silica contents (basaltic andesite to rhyolite with ~55–74 wt% SiO_2 ; Tables 1 and 2) and radiogenic strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr} = \sim 0.705\text{--}0.712$, Table 1; Davidson et al., 1991; Davidson and de Silva, 1995; Folkes et al., 2013; Kay et al., 2011; Trumbull et al., 1999).

We use two proxies for $f\text{O}_2$ to evaluate the oxidation state of arc magmas from the CVZ: the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio (where $\Sigma\text{Fe} = \text{Fe}^{3+} + \text{Fe}^{2+}$) as determined on bulk rocks by wet chemistry or as measured directly in glassy melt inclusions using Fe K-edge X-ray absorption near-edge structure (XANES) spectroscopy, and the $f\text{O}_2$ determined from magnetite-ilmenite pairs. We provide quantitative documentation of the effect of differentiation on the $f\text{O}_2$ s recorded by CVZ magmas. We explore the extent to which crustal processes versus modifications to the mantle wedge may be responsible for inducing calc-alkaline magmatism.

2. Geologic background

The present N–S oriented cordillera of the Andes is the result of ~200 My of subduction of the Nazca plate (Fig. 1). The Central Volcanic Zone, or CVZ, of the Central Andes lies above exceptionally thick crust (up to 80 km; Beck et al., 1996; Yuan et al., 2002; Appendix A.1), created by horizontal shortening of a thermally softened lithosphere, which uplifted the Altiplano–Puna plateau (Allmendinger et al., 1997; Isacks, 1988). Intense and voluminous caldera-forming eruptions formed the Altiplano–Puna Volcanic Complex (APVC; de Silva, 1989a; de Silva et al., 2006). The dominantly dacitic ignimbrites throughout the Central Andean Neogene Ignimbrite Province, with basaltic andesite as a minor component, belong to a high-K, calc-alkaline suite and have chemical and isotopic characteristics that suggest subduction-related mafic magmas variably contaminated by continental crust, the most contaminated being those in the APVC (de Silva et al., 2006; Folkes et al., 2013; Kay et al., 2011; Ort et al., 1996; Appendix A.1). “Baseline” isotopic compositions of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ~0.706 and $^{144}\text{Nd}/^{143}\text{Nd}$ ratios of ~0.5124 record minimal crustal contamination (Burns et al., 2015; Davidson et al., 1991; de Silva et al., 2006; Hildreth and Moorbath, 1988). Extension of the baseline compositions to more “crustal” values indicates the significant leverage that continental crust exerts on isotopic compositions, with some extreme CVZ magmas nearing assimilated compositions (Fig. 2; de Silva, 1989b; Hawkesworth et al., 1982; Klerx et al., 1977).

3. Geochemistry of CVZ magmas and sample selection

We chose samples that represented the maximum possible range of crustal differentiation in the CVZ. The samples represent 10 different volcanic centers and capture a large range of eruptive styles and products, compositions, and crystal contents (Table 1; Table A.1). We selected petrographically and geochemically well-

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