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Sulfur isotopic compositions of deep arc cumulates

Cin-Ty A. Lee [a,*], Monica Erdman [a,b], Wenbo Yang [c], Lynn Ingram [d], Emily J. Chin [a,e], Donald J. DePaolo [d]

[a] Department of Earth Science, MS-126, Rice University, 6100 Main St., Houston, TX 77005, USA
[b] United States Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025, USA
[c] Center for Stable Isotope Biogeochemistry, University of California, Berkeley, CA 94720-4767, USA
[d] Department of Earth and Planetary Sciences, University of California, Berkeley, CA 94720-4767, USA
[e] Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, Mail Code 0212, La Jolla, CA 92093-0212, USA

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ABSTRACT

Heavy sulfur isotopic compositions of arc lavas suggest a seawater component in the sulfur budget of arc lavas, but whether the seawater signature derives from the subducting slab or from magma interactions with lithologies in the upper plate is unclear. To see through the effects of degassing or crustal processing, a study was conducted on the S isotopic composition of deep arc cumulates from 45–90 km beneath the Sierra Nevada batholith in California, a Cretaceous continental arc. These cumulates represent the crystal line of descent from magmatic differentiation of hydrous arc basalts. The deepest (up to 60–90 km) and most primitive cumulates are low in Fe and have high molar Mg/(Mg + Fe), whereas the shallow and more evolved cumulates are high in Fe and have low Mg/(Mg + Fe). Bulk rock δ^{34}S correlates with Fe and negatively with Mg/(Mg + Fe). The most primitive cumulates are isotopically similar to the Earth's mantle whereas the more evolved cumulates are heavier by 6‰ in the direction of seawater sulfate. The mantle-like S isotopic signatures of the primitive cumulates indicate that the contribution of slab-derived sulfate to arc lavas may not be as large as widely thought. Heavy S isotopic signatures are seen only in the evolved arc cumulates, which suggests that the seawater signature of arc lavas may not all derive directly from the slab, but perhaps during magma interaction with pre-arc crust. In continental arcs, pre-arc crust is dominated by accreted marine metasediments and metabasalts, and in island arcs, by seawater altered oceanic crust in the upper plate. The limited contribution of slab sulfate to the mantle source of Sierran arc magmas, if generalizable, suggests that sulfate in the subducting slab is efficiently released well before the arc magmatic front. Such a scenario would be consistent with the higher solubility of sulfate in aqueous fluids compared to that of sulfide. In summary, it is suggested here that the upper plate, in the form of seawater altered crust and sediments, may be as or more important for the sulfur budget in arc magmas than the subducting slab. Early loss of sulfate from the slab during subduction suggests that the dominant S species transported to the deep mantle is in the reduced form – sulfide.

1. Introduction

Sulfur (S) exhibits a wide range of valence states (−2 to +6), allowing it to behave as an electron acceptor or donor depending on the chemical environment. This versatility makes S an important element in geochemistry and biology. For example, the oxidized form – sulfate ion (S^{6+} in SO_4^{2-}) is a source of O_2 if it can be reduced to sulfide (S^{2-}). Thus, S is a potential driver of the redox reactions that dictate the mobility of metals. Understanding S geochemistry is critical to understanding the origin of ore deposits, the evolution of O_2 in the atmosphere and marine environment, the pathways of biogeochemical processes, and climate change (Holland, 1973). Of interest is how S cycles between the endogenic (crust, mantle and core) and exogenic systems (ocean, atmosphere and biosphere) of the Earth. The plethora of S isotope studies in marine environments over the last several decades has significantly advanced our understanding of S cycling within the exogenic system (Holland, 1973). However, our understanding of how much exogenic S and what type of S – reduced or oxidized – is recycled back into the endogenic system through subduction zones and returned to the atmosphere through arc volcanoes is comparatively less complete (Wallace and Edmonds, 2011).

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* Corresponding author.
E-mail address: ctlee@rice.edu (C.-T.A. Lee).

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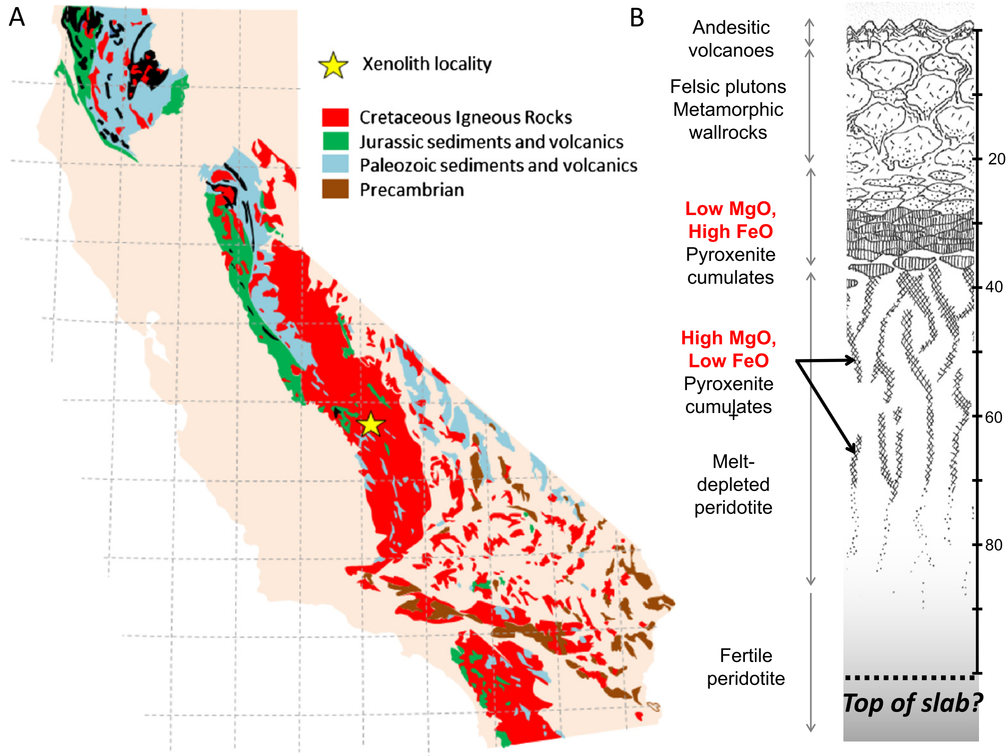

Fig. 1. A. Modified geologic map of California (Jennings, 1958) showing Cretaceous batholithic rocks and outcrops of pre-Cretaceous metasedimentary and metavolcanic rocks. Location of Miocene xenolith-bearing volcano (Big Creek diatreme) is shown with a star. B. Schematic cross-section of the batholith modified (Ducea and Saleeby, 1998; Lee, 2014).

While it is widely thought that seawater sulfate is transported into subduction zones via marine sediments and hydrothermally altered oceanic crust, the fate of such sulfate is unclear. One possibility is that sulfate is subducted deep into the mantle, potentially oxidizing the sub-arc mantle wedge, enriching it in S and culminating in the release of oxidized S during volcanic eruptions (Kelley and Cottrell, 2009; Wallace and Edmonds, 2011). Heavy S isotopic signatures of sulfides in eclogites have been argued to indicate that seawater-derived sulfate survives deep into the subduction zone and is hence available for metasomatizing the subarc mantle wedge (Evans et al., 2014). Addition of seawater sulfate into the mantle wedge could explain why the SO_2 flux in arc volcanoes is larger than that at mid-ocean ridges (Allard et al., 1994; Luhr et al., 1984; Wallace and Edmonds, 2011) and why the S isotopic composition of arc basalts ($\delta^{34}S$) are slightly heavy in the direction seawater sulfate (Alt et al., 1993; De Hoog et al., 2001).

However, the evidence that sub-arc mantle is substantially influenced by sulfate is not unequivocal. While some sub-arc mantle xenoliths appear to be oxidized (McInnes et al., 2001) and field evidence for sulfate reduction in mantle rocks has been documented (Rielli et al., 2017), peridotitic mantle has also been shown to have been metasomatized by sulfide-bearing fluids or melts or even reducing agents, such as methane (Ishimaru et al., 2009; Song et al., 2009; Wang et al., 2008). Cu contents of primitive arc magmas are generally similar to the low values of mid-ocean ridge basalts, which may suggest sulfide-saturation in the mantle source (Jenner et al., 2010; Lee et al., 2012). Finally, the S isotopic composition of arc melt inclusions can be highly variable, ranging from mantle-like values to values trending towards seawater values (Mandeville et al., 2009a), suggesting that there may be multiple origins of S in arc magmas.

Upper plate processes may also play important roles in controlling magma redox and S systematics (Tomkins et al., 2012). Elevated S contents can be inherited from interaction with altered crust or metasediments in the upper plate (Carroll and Rutherford, 1987) or can be an artifact of accumulation of volatiles at the tops of magma chambers (Wallace and Gerlach, 1994). Heavy S isotopic compositions can be generated by shallow-level degassing (Mandeville et al., 2009b; Metrich and Mandeville, 2010) and crustal assimilation. Indeed, S isotopes in plutonic belts have been shown to correlate spatially with the composition of metamorphic wallrocks (Ishihara and Sasaki, 1989). An upper plate contribution to volatiles has also been suggested for continental arc volcanoes that intersect ancient carbonate platforms (Carter and Dasgupta, 2015; Deegan et al., 2010; Lee et al., 2013). Crustal carbonate-intersecting volcanoes tend to have heavier carbon isotopes, suggesting that crustal contributions to the carbon budget of arcs can be high (Aiuppa et al., 2017; Mason et al., 2017). To what extent is the S budget of volcanoes influenced by crust-bound S?

To explore the influence of upper plate processes, we examine the S isotopic systematics of deep arc cumulates using a case study of Cretaceous continental arc cumulates brought to the surface as xenoliths in late Miocene alkali basalts in the Sierra Nevada batholith, California (USA) (Fig. 1A). These cumulates are petrogenetically associated with Sierran continental arc magmatism and record equilibration pressures equivalent to depths of 40–90 km (Chin et al., 2012; Ducea and Saleeby, 1996; Lee et al., 2006). They represent the deepest and most primitive differentiates of an arc, sampling a section from the top of the sub-arc mantle wedge to the lower crust, and providing an opportunity to explore the S isotopic composition of arc magmas before they have undergone significant degassing or interaction with the upper plate (Fig. 1B). In addition to the cumulate study, we also analyzed the bulk S isotopic composition of Hawaiian lavas and Franciscan eclogites to evaluate the extent to which newly formed crust can be overprinted by seawater or subducted oceanic crust can retain seawater sulfate.