Sulfur in the slab: A sulfur-isotopes and thermodynamic-modeling perspective from exhumed terranes

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Sulfur is a key element in the subduction zone-volcanic arc system; however, the mechanism(s) that recycle sulfur from the slab into the overlying volcanic arc are debated. Here we summarize recent advances in quantifying this component of the deep sulfur cycle. First, primary metamorphic or inherited sulfides in oceanic-type eclogites are only rarely observed as inclusions and are typically absent from the rock matrix. Additionally, sulfides are relatively common in rocks metasomatized at the slab-mantle interface by slab-derived fluids during exhumation. Combined, these two observations suggest that sulfur loss from subducted mafic crust is relatively efficient. Thermodynamic modeling in Perple_X using the Holland and Powell (2011) database combined with the Deep Earth Water model suggests that the efficiency and speciation of sulfur loss varies depending on the degree of seafloor alteration prior to subduction and the geothermal gradient of the slab. In relatively cold subduction zones, such as Honshu, slab-fluids derived from subducted mafic crust are predicted to exhibit elevated concentrations of HSO_4^-, SO_4^{2-}, HSO_3^-, and $CaSO_{4(aq)}$, whereas hot subduction zones, such as Cascadia, are predicted to produce slab fluids enriched in HS^- and H_2S at lower pressures. The oxidation of sulfur expelled from subducted pyrite is balanced by the reduction of Fe^{3+} to Fe^{2+}, consistent with the low Fe^{3+}/SFe of exhumed eclogites relative to blueschists and altered oceanic crust. Where oxidized S-bearing fluids are produced, they are anticipated to interact with more reduced rocks at the slab-mantle interface and within the mantle wedge, resulting in sulfide precipitation and significant isotopic fractionation. The $\delta^{34}S$ values of slab fluids are estimated to fall between -11 and +8 ‰. Rayleigh fractionation during progressive fluid-rock interaction results in fractionations of tens of per mil as oxidized species are depleted and sulfides are precipitated, resulting in $\delta^{34}S$ values of sulfides that easily span the -21.7 to +13.9 ‰ range observed in metasomatic sulfides in exhumed high-pressure rocks. However, in subduction zones where reduced species prevail, the S isotopic signature of slab fluids is expected to reflect their source and will exhibit a narrower range in $\delta^{34}S$ values. As a result, the $\delta^{34}S$ values measured in arc magmas may not always be a reliable indicator of the contribution of different components of the slab, such as sediments vs. AOC. Additionally, the impact of S recycling on the oxygen fugacity of arc magmas is expected to vary both spatially and temporally throughout Earth history.

How to cite: Walters, J., Cruz-Uribe, A., and Marschall, H.: Sulfur in the slab: A sulfur-isotopes and thermodynamic-modeling perspective from exhumed terranes, EGU General Assembly 2022, Vienna, Austria, 23–27 May 2022, EGU22-11697, https://doi.org/10.5194/egusphere-egu22-11697, 2022.