

# Mantle wedge oxidation by sulfate species via fluid-rock reaction

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Arc magmas produced above subduction zones are generally more oxidized than magmas from other tectonic settings, but there is considerable debate surrounding the causes for this signature. Recent evidence suggests that the abundance of oxidized sulfur species in slab fluids controls the oxidation rate of the mantle wedge [1], but an experimentally based calibration of sulfur solubility at subduction zone conditions has been lacking. Here we used a new aqueous sulfur speciation and solubility model calibrated with experimental anhydrite solubilities at high pressures and temperatures [2]. We carried out chemical mass transfer calculations modeling the irreversible reaction of slab fluids encountering the mantle wedge. Exiting the slab, the fluids are in equilibrium with eclogitic, mafic subducted lithologies at temperatures up to 650°C. They react with peridotite in the mantle wedge in a temperature gradient up to 950°C. Hot slab fluids initially in equilibrium with pyrite at FMQ+2 at 650°C retain their oxidized signature as they react up the thermal gradient in the mantle wedge. They overwhelm the oxidation state of the rock even at low fluid-rock ratios of ~0.1 (Fig. 1a). In contrast, more dilute, S-poor fluids at FMQ+2 are reduced upon reaction with the mantle wedge at identical conditions. Fluids initially less oxidized (e.g. FMQ+1) also have lower sulfur solubility and are thus also reduced to greater extents (Fig. 1b). The solubility of sulfate species is enhanced at higher pressures, such that colder slabs could also release oxidized, S-rich fluids at deeper levels (Fig. 1c). During heating in the mantle wedge, fluids become undersaturated with initial mantle FeS (~200 ppm S) and dissolve it. Therefore, sulfur in hydrous primitive magmas is a mixture of slab-derived and mantle S, and its  $\delta^{34}\text{S}$  signature depends on the slab thermal profile and fluid-rock ratio, as well as the nature of subducted sediments. Oxidized, S-rich slab fluids can better retain their oxidized signatures and initial  $\delta^{34}\text{S}$  that are ultimately transferred to arc magmas.

[1] Padrón-Navarta et al., 2023, *Nature Geoscience*

[2] Beaudry & Sverjensky, 2022, *Goldschmidt Conference*

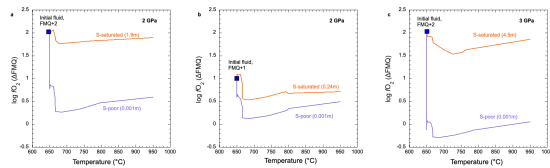


Figure 1: Model slab fluids reacting with mantle peridotite at 2 GPa (a,b) and 3 GPa (c). Water/rock = 0.1.