

Mantle oxidation driven by variable sulfur release during subduction

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Quantifying mantle oxygen fugacity (fO_2) is essential to constrain the physics of Earth's interior; the mineralogy and composition of the mantle govern material properties such as rheology and density. Subduction has long been speculated to influence mantle fO_2 by introducing altered oceanic crust (AOC), hydrated and oxidized at mid-ocean ridges, into the mantle; however, a clear quantitative link between oxidized slab components and mantle fO_2 heterogeneities remain elusive. As the SSO buffer ($FeS + 2O_2 = FeO + SO_3$) occurs at approximately QFM+2, oxidized sulfur-bearing fluids possess great leverage with which to oxidize the subarc mantle at subduction zones.

Here we present thermodynamic models for MORB and AOC created in Perple_X utilizing the combined thermodynamic databases of [1] and [2] that predict the volume and speciation of sulfur lost from subducting AOC. Stable sulfur-bearing metamorphic assemblages predicted over a P-T range of 1.5-3.5 GPa and 500-800 °C for average AOC show sulfur oxidation with increasing depth. Transitions from pyrrhotite to pyrite to anhydrite are observed with increasing P-T. A model for average MORB exhibits higher pressures for the pyrite- and anhydrite-in reactions, suggesting that prograde sulfur oxidation varies as a function of seafloor alteration. Sulfur oxidation is balanced by Fe^{3+} reduction, resulting in a nearly 50 % decrease in $Fe^{3+}/\Sigma Fe$ in AOC over the interval 500-750 °C.

Sulfur concentration and speciation in slab fluids are found to vary as a function of subduction zone thermal structure. In models that allow fluids to fractionate along an open system P-T path, nearly 32 % more sulfur is lost along a 'cold' path (i.e., Honshu) than a 'hot' path (i.e., Cascadia). We predict larger sulfur fluxes in cold subduction zones, due to the coincident depths of the major dehydration reactions with the sulfide-sulfate transition. Hot subduction zones should exhibit shallow reduced and deep oxidized sulfur fluxes, whereas cold subduction zones will be dominated by the release of oxidized sulfur.

[1] Holland & Powell (2011) JMG

[2] Servjensky et al. (2014) GCA

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