

Fast mantle wedge oxidation promoted by sulfur disproportionation in deep COHS Slab fluids

ANDREA MAFFEIS¹, MARIA LUCE FREZZOTTI¹, JAMES
A. D. CONNOLLY², DANIELE CASTELLI³ AND SIMONA
FERRANDO³

¹Università degli Studi di Milano - Bicocca

²Institute of Geochemistry and Petrology - ETH

³Università degli Studi di Torino

Sulfur degassing at volcanic arcs is thought to involve dissolved S⁶⁺ released by subduction-zone fluids, which oxidise the sub-arc mantle alongside carbon. However, the mechanisms of sulfur speciation and dissolution in subduction fluids at subarc depths remain unclear. We apply electrolytic fluid thermodynamics to model the dissolution behaviour of pyrite during fluid-rock interaction in meta-carbonate sediments. Modelling spanned sub-arc conditions up to 4.3 GPa, 730°C and redox $\Delta\text{FMQ}-1$ to $\Delta\text{FMQ}+1$ (FMQ, fayalite-magnetite-quartz). At subarc depth and at the redox conditions of the FMQ oxygen buffer, pyrite dissolution releases oxidised S in fluids by disproportionation into sulfate, bisulfite, and sulfide species. This behaviour persists across various lithologies, such as serpentinites and altered oceanic crust. Further open system modelling, simulating serpentinite-derived and altered oceanic crust-derived fluids infiltration in sediments sitting atop the downgoing slab, shows how S speciation remains disproportionated, while the fluid itself becomes more oxidising. Finally, a global mass balance of fluid and redox budget flux shows that, depending on the slab's thermal state, such fluids are capable of oxidising the sub-arc mantle within a few million years from subduction initiation. These findings [1] indicate that oxidised, sulfur-rich COHS fluids form within subducting slabs at depths greater than 100 km independent from slab redox state and that sulfur can be more effective than the concomitantly dissolved carbon at oxidising the mantle wedge, especially when carbonates are stable.

[1] Maffei, Frezzotti, Connolly, Castelli & Ferrando (2024), *Science Advances* 10(12), eadj2770