

## Modulated redox capacity of serpentinite-derived fluids

JOSÉ ALBERTO PADRÓN-NAVARTA<sup>1</sup>, VICENTE LOPEZ SANCHEZ-VIZCAINO<sup>2</sup>, MANUEL D. MENZEL<sup>3</sup>, MARÍA TERESA GÓMEZ-PUGNAIRE<sup>4</sup> AND CARLOS J. GARRIDO<sup>1</sup>

<sup>1</sup>Instituto Andaluz de Ciencias de la Tierra (IACT/CSIC)

<sup>2</sup>Universidad de Jaen

<sup>3</sup>Instituto Andaluz de Ciencias de la Tierra (CSIC-IACT)

<sup>4</sup>Universidad de Granada

Presenting Author: [alberto.padron@csic.es](mailto:alberto.padron@csic.es)

The formation of primary arc basalts during subduction is attributed to the high-pressure dehydration of serpentinite (deserpentinisation), which generates fluids that flux and melt the overlying mantle wedge. These basalts are more oxidised than their mid-ocean ridge counterparts. At the slab surface of current subduction zones, these deserpentinisation fluids are intrinsically oxidised but, owing to the low sulphur content of subducted serpentinite, they only result in a low mantle-wedge oxidation rate, which cannot account for the oxidised source of arc basalts. Through a combination of natural observations and thermodynamic modelling, we show that infiltration of sediment-derived fluids can alter the oxidation capacity of deserpentinisation slab fluids, providing an explanation for the oxidised nature of arc volcanism.

The deserpentinisation oxidation capacity is mainly influenced by the stability and abundance of dissolved oxidised aqueous species of redox-sensitive elements, notably sulphate, rather than the oxidation state of the sediment. Infiltration of CH<sub>4</sub>-bearing fluids derived from graphite-bearing sediment reduces the oxidant capacity of deserpentinisation fluids, leading to a relatively low  $fO_2$  observed in natural metaperidotite. On the other hand, infiltration of sulphate-CO<sub>2</sub>-bearing, sediment-derived fluids results in a high oxidation capacity of deserpentinisation fluids in cold and hot subduction zones, leading to a global mantle-wedge oxidation rate of 3.5 km<sup>3</sup>·yr<sup>-1</sup>. Therefore, these slab fluids can oxidize the mantle wedge at a rate similar to that of arc basalt generation, explaining the oxidised nature of arc volcanism. The findings suggest that sediment-derived fluids (and potentially also fluids derived from the Altered Oceanic Crust) can significantly modulate the oxidation capacity of deserpentinisation slab fluids, highlighting the importance of slab fluid-mixing in the volatile recycling in the subduction zone system.

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