

## Oxygen breath of subduction zones revealed by arsenic in serpentinite

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Subduction zones are fascinating redox factories on Earth that scavenge or release water, oxygen, hydrogen, sulfur and carbon. When, why, and how much subduction zones “breathe” in and out volatile elements remain, however, poorly constrained. This gap of knowledge is owing to the lack of in situ geochemical tracers that could be able to record, during the different subduction stages, the evolution of redox conditions.

We studied, using X-ray absorption spectroscopy (XAS), the chemical and redox state of arsenic in the serpentinites of the Tso Moriri massive, NW Himalaya (Fig. 1a), that was a subduction zone 40-50 My ago. These rocks were exhumed from about 100 km depth during orogenesis and bear a precious witness of the deep subduction phenomena [1]. Our measurements reveal remarkably contrasting redox speciation, from arsenide ( $\text{As}^{3-}$ ) to arsenite ( $\text{As}^{3+}$ ) and arsenate ( $\text{As}^{5+}$ ) (Fig. 1b) We combined these findings with in-situ XAS experiments in a diamond-anvil cell, complementary analytical methods [2], thermodynamic modeling [3], and the well-constrained geodynamic history of these rocks [1], to reconstruct the extraordinary redox travel of arsenic in the subduction zone and to use this element as an oxygen probe [4].

Our results show that upon early serpentinisation of mantle peridotite, arsenic was scavenged from the fluid and dragged down as insoluble nickel arsenide. Partial deserpentinisation close to the peak metamorphism (550–650 °C) resulted in oxidative dissolution of arsenide to aqueous  $\text{As}^{3+}$  and  $\text{As}^{5+}$  and their non-specific intake by antigorite. The  $\text{As}^{5+}/\text{As}^{3+}$  ratios (0.1–10) analyzed in the mineral are  $\sim 10^4$  times higher on average than predicted assuming bulk-system thermodynamic equilibrium. These findings reflect a transient out-of-equilibrium release of highly oxidized fluids, with  $f_{\text{O}_2}$  reaching 10 log units above the fayalite-magnetite-quartz buffer (FMQ+10). Arsenic in serpentinite is thus a sensitive record of subduction redox

dynamics inaccessible when using traditional equilibrium approaches applied to bulk fluid-mineral systems.

[1] Guillot et al. (2008) *Tectonophysics* 451:225–241; [2] Borisova et al. (2021) *Front Earth Sci* 9:640464; [3] Perfetti et al. (2008) *Geochim Cosmochim Acta* 72:713–731; [4] Pokrovski et al. (2022) *Geochem Pesp Let* 22:36–41.

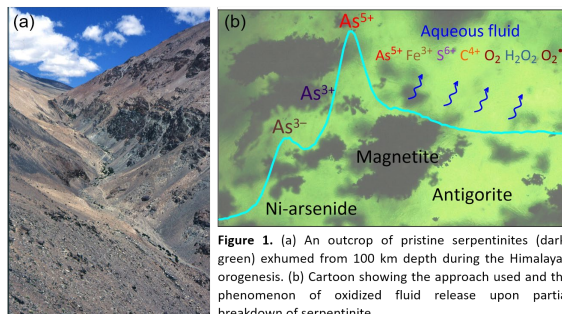


Figure 1. (a) An outcrop of pristine serpentinites (dark-green) exhumed from 100 km depth during the Himalayan orogenesis. (b) Cartoon showing the approach used and the phenomenon of oxidized fluid release upon partial breakdown of serpentinite.