

FLUIDS IN THE CRUST

**Experimental constraints on fluid-rock reactions during incipient serpentinization of harzburgite†**

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**ABSTRACT**

The exposure of mantle peridotite to water at crustal levels leads to a cascade of interconnected dissolution-precipitation and reduction-oxidation reactions—a process referred to as serpentinization. These reactions have major implications for microbial life through the provision of hydrogen (H<sub>2</sub>). To simulate incipient serpentinization under well-constrained conditions, we reacted centimeter-sized pieces of uncrushed harzburgite with chemically modified seawater at 300 °C and 35 MPa for ca. 1.5 yr (13441 h), monitored changes in fluid chemistry over time, and examined the secondary mineralogy at the termination of the experiment. Approximately 4 mol% of the protolith underwent alteration forming serpentine, accessory magnetite, chlorite, and traces of calcite and heazlewoodite. Alteration textures bear remarkable similarities to those found in partially serpentinized abyssal peridotites. Neither brucite nor talc precipitated during the experiment. Given that the starting material contained ~4 times more olivine than orthopyroxene on a molar basis, mass balance requires that dissolution of orthopyroxene was significantly faster than dissolution of olivine. Coupled mass transfer of dissolved Si, Mg, and H<sup>+</sup> between olivine and orthopyroxene reaction fronts was driven by steep activity gradients and facilitated the precipitation of serpentine. Hydrogen was released in significant amounts throughout the entire experiment; however, the H<sub>2</sub> release rate decreased with time. Serpentinization consumed water but did not release significant amounts of dissolved species (other than H<sub>2</sub>) suggesting that incipient hydration reactions involved a volume increase of ~40%. The reduced access of water to fresh olivine surfaces due to filling of fractures and coating of primary minerals with alteration products led to decreased rates of serpentinization and H<sub>2</sub> release. While this concept might seem at odds with completely serpentinized seafloor peridotites, reaction-driven fracturing offers an intriguing solution to the seemingly self-limiting nature of serpentinization. Indeed, the reacted sample revealed several textural features diagnostic of incipient reaction-driven fracturing. We conclude that fracturing must have far reaching impacts on the rates of serpentinization and H<sub>2</sub> release in peridotite-hosted hydrothermal systems.

**Keywords:** Serpentinization, phase relations, reaction rates, reaction pathways, fracturing, hydrogen, hydrothermal experiment