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Redox Controls and Reaction Pathways during Serpentinization of Abyssal Peridotite

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The aqueous alteration of ultramafic rocks liberates substantial amounts of hydrogen via the oxidation of ferrous iron in primary minerals to ferric iron in secondary minerals; however, the underlying mechanisms of this process remain poorly understood. We examined partly to completely serpentinized peridotites from continental rifted margins, mid-ocean ridges, and fore-arc settings of subduction zones recovered during DSDP/ODP Legs 82, 107, 125, 147, 149, 153, 173, 195, 209, 210, and 304/305 using a variety of microscopic and spectroscopic methods. We merged petrographic observations and chemical analyses with thermodynamic reaction path models and hydrothermal experiments to establish basic conceptual mechanisms of peridotite-seawater interactions. In principle, the complex variations in temperature, host-rock composition, water-to-rock ratio, and reaction kinetics are recorded by the secondary mineralogy. Our results suggest that high temperature (>250°C) serpentinization of olivine at low water-to-rock ratios leads to the formation of magnetite and serpentine together with relatively Fe-poor brucite in mesh texture, and thus to strongly reducing conditions (e.g., at Leg 153). If serpentinization of peridotite proceeds at low temperatures, production of magnetite is limited and brucite generally Fe-richer (e.g., Leg 173), which results in somewhat less reducing conditions. Serpentinization of orthopyroxene-rich lithologies does not generate significant amounts of magnetite (unless it undergoes post-serpentinization oxidation), while serpentine in bastite texture is Fe-rich. In addition to protolith composition, the relative dissolution kinetics of olivine and orthopyroxene can influence the silica activity during serpentinization of peridotite and thus control whether the assemblage brucite-serpentine-clinopyroxene-magnetite or serpentine-talc-tremolite-chlorite is stable. The former assemblage is associated with strongly reducing, high pH, silica poor and Ca rich fluids whereas the latter assemblage reflects higher Si activities, lower pH and less reducing conditions. If olivine and orthopyroxene dissolve at similar rates the assemblage serpentine-magnetite is stable. The interacting fluid is strongly reducing, but the pH and the Si activities are buffered to intermediate levels relative to the aforementioned assemblages. These simple relations can be used to unravel approximate reaction sequences during serpentinization of dunite, harzburgite, lherzolite, and pyroxenite.