A seawater throttle on hydrothermal Fe oxidation in the ancient oceanic lithosphere

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Fe oxidation and coupled hydrogen (H_2) generation during seafloor serpentinization are thought to have provided a principle feedstock for earth's earliest lifeforms and a pivotal counterbalance to photosynthetic oxygen (O_2) production following its metabolic evolution. However, the effect of differing ancient seawater chemistry on these fluxes and their seafloor expression remain unexplored, due to historically limited constraints on ancient seawater chemistry and the common assumption that seafloor hydrothermal systems are lithologically dominated rather than hydrogeochemically mediated. In recent years, however, quantitative estimates of the makeup of paleoseawater have increasingly come into focus[1-3] as field and experimental measurements have demonstrated important kinetic limitations on serpentinization reactions at temperatures representative of modern off-axis hydrothermal systems[4]. Here, we integrate recently published constraints on ancient seawater chemistry together with kinetic, thermodynamic and crystallographic constraints on water-rock interaction and redox evolution into a reactive transport model of early earth serpentinization. The results indicate that the chemical characteristics of ancient seawater would have limited the extent of Fe oxidation during serpentinization. This "seawater throttle" on Fe oxidation during serpentinization would have diminished the fluxes of H_2 from the oceanic lithosphere, with various implications for the coupled evolution of the planet's early biosphere and atmosphere. Although the rock record available for comparison is limited, these calculations qualitatively agree with observations from this time.

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[3]Stefurak et al. *Bull. Geol. Soc. Am.* 127, 1090–1107 (2015).
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