



# Low temperature hydrogen production during experimental hydration of partially-serpentinized dunite

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## Abstract

Dissolved hydrogen is common in mafic and ultramafic aquifers; however, the water/rock reactions that give rise to hydrogen production at near-surface temperatures are enigmatic. Similarly, mineral hydration experiments have not yet unequivocally demonstrated whether H<sub>2</sub> can be produced at low-temperatures at significant rates from reaction of aqueous fluids with basalts and peridotites for prolonged amounts of time. We conducted laboratory-based water/rock reactions between partially serpentinized Oman dunite and a simulated Oman rainwater (RW) media, as well as a simulated seawater (SW) media, to quantify H<sub>2</sub> generation rates at 100 °C. Throughout more than 9 months of water/rock reaction, extensive hydrogen production and consumption were observed in RW and SW media. In the first 24 h of reaction in anoxic fluids containing only dissolved N<sub>2</sub> and CO<sub>2</sub>, the room-temperature pH in both RW and SW media increased from 6.5 to ~9, and the average pH then remained relatively constant at pH 8.5 (±0.5 pH) for the duration of the experiments. We also measured some of the highest hydrogen concentrations observed in experimental low-temperature serpentinization reactions. The maximum measured H<sub>2</sub> concentrations in SW media were 470 nmol H<sub>2</sub> per g mineral after ~3 months, while RW media H<sub>2</sub> concentrations reached 280 nmol/g H<sub>2</sub> after ~3 months. After reaching micromolar dissolved H<sub>2(aq)</sub>, the H<sub>2</sub> concentrations notably declined, and CO<sub>2</sub> was almost fully consumed. We measured the formation of formate (up to 98 μM) and acetate (up to 91 μM) associated with a drawdown of H<sub>2</sub> and CO<sub>2</sub> in the experiments. No CH<sub>4</sub> or carbonate formation was observed. To identify reactions giving rise to low-temperature hydrogen production, the mineralogy and oxidation state of the Fe-bearing species in the dunite were extensively characterized before and after reaction using Raman spectroscopy, Quantitative Evaluation of Minerals by SCANing electron microscopy (QEMSCAN), powder X-ray diffraction (XRD), magnetic susceptibility, scanning electron microscopy (SEM), and Fe K-edge X-ray absorption near edge structure (XANES) spectroscopic techniques. The mineralogy of the solid starting material was dominated by olivine and serpentine with minor brucite, pyroxene and spinel. After reaction, additional serpentine and magnetite could be detected as reaction products, and pre-existing brucite was consumed. No changes were observed in the abundance or grain sizes of olivine or pyroxene. Thus, we propose that the destabilization of Fe(II)-bearing brucite and the subsequent oxidation of the aqueous Fe(II) to form magnetite and Fe(III)-rich serpentine give rise to H<sub>2</sub> production at 100 °C. This work demonstrates that dissolved hydrogen and low molecular weight organic acids can be produced by the reaction of labile Fe

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(II)-bearing minerals generated during a prior stage of water/rock reactions. In particular, progressive alteration of partially-serpentinized peridotites containing brucite may generate sufficient electron donors to fuel in-situ subsurface microbial activity.

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## 1. INTRODUCTION

Serpentinization, the hydration and oxidation reaction of ultramafic rocks and minerals, can produce hydrogen at low temperatures which can support H<sub>2</sub>-fueled microbial life (Sleep et al., 2004; Nealon et al., 2005; Mayhew et al., 2013). Low-temperature reactions can be classified as those occurring  $\leq 122$  °C (Takai et al., 2008), which is the highest temperature of observed microbial growth. Serpentinization reactions are predicted to produce less hydrogen at temperatures relevant for microbial life, but still enough to sustain subsurface microbial ecosystems, which can utilize H<sub>2</sub> concentrations as low as 13 nM (Kral et al., 1998; Nealon et al., 2005). H<sub>2</sub>-fueled metabolisms are diverse and include anaerobic methanotrophy, fermentation, sulfate reduction and hydrogen oxidation tied to iron reduction (Schrenk et al., 2013). H<sub>2</sub> produced by serpentinization reactions may have fueled the first life on Earth at low-temperature off-axis hydrothermal fields (Russell et al., 2010, 2013; Shibuya et al., 2016). Additionally, serpentinization reactions have likely occurred on Enceladus and Mars, which may provide a favorable environment for H<sub>2</sub>-utilizing microbial life (Ehlmann et al., 2010; Glein et al., 2015; Sekine et al., 2015).

However, the mechanisms and reaction pathways giving rise to hydrogen production at low temperatures are unclear (Stevens and McKinley, 1995; Anderson et al., 1998; Neubeck et al., 2011, 2014; Mayhew et al., 2013; Okland et al., 2014; Telling et al., 2015), whereas high temperature (>200 °C) hydrogen production is well-characterized through both experimental and modeling efforts (Fyfe, 1974; McCollom and Seewald, 2001; McCollom and Bach, 2009; Klein et al., 2009, 2013, 2015; Evans et al., 2009; Malvoisin et al., 2012a,b; Frost et al., 2013; McCollom et al., 2016). Thus, further work on low-temperature serpentinization and associated hydrogen production is necessary to better constrain reaction pathways and mechanisms (Mayhew et al., 2013; Bach, 2016; McCollom and Donaldson, 2016).

Although extensive thermodynamic modeling of hydrogen production has been conducted at high temperatures, these results cannot be easily extrapolated to lower temperatures. Several thermodynamic models have been used to infer that water/rock reactions at low temperatures will generate much less hydrogen than at temperatures from 200 to 350 °C (McCollom and Bach, 2009; Klein et al., 2009, 2013). Hydrogen production at temperatures <120 °C is predicted to strongly decrease because Fe(II) released from olivine will be sequestered into secondary brucite, resulting in less Fe oxidation. Magnetite formation is also thermodynamically inhibited at low temperatures

(McCollom and Bach, 2009; Klein et al., 2013). Instead, the formation of Fe(III)-rich serpentine may be the central reaction accommodating low-temperature hydrogen generation. Thermodynamic models also assume systems reach a state of equilibrium, and this may not occur during fluid flow through peridotite aquifers (Paukert et al., 2012). Also, the kinetics and mechanisms of the key mineral dissolution, precipitation and Fe(II)-oxidation reactions are poorly constrained, along with the thermodynamic data for Fe(III) secondary phases that form at low temperatures.

Although recent kinetic-thermodynamic modeling of reactions between peridotite and water at 25 °C (Bach, 2016) addresses some of these issues, it is clear that these models need to be experimentally verified. Further mechanistic studies are needed to reveal the rates and reactions involved in H<sub>2</sub> production during low temperature peridotite alteration. New models by Bach (2016) better capture the complexity of these low-temperature reactions by allowing the precipitation of several possible Fe(III) reaction products to accommodate H<sub>2</sub> production. Notably, these new models predict that more H<sub>2</sub> could be produced at low temperatures than has been observed experimentally (e.g. in Mayhew et al. (2013) and Neubeck et al. (2011), etc.). Experiments coupled with new models may help to explain how continental ophiolite systems contain high concentrations of dissolved hydrogen at near surface temperatures (Neal and Stanger, 1983; Abrajano et al., 1990; Etiope et al., 2011; Morrill et al., 2013; Szponar et al., 2013; Suda et al., 2014; Miller et al., 2016).

Several experimental studies of water/rock reactions have investigated the rates and extent of low-temperature H<sub>2</sub> generation (Stevens and McKinley, 1995; Anderson et al., 1998; Neubeck et al., 2011, 2014; Mayhew et al., 2013; Okland et al., 2014; Telling et al., 2015), yet they have encountered numerous challenges and have produced inconsistent results (Table 1). It is difficult to reproduce results as a variety of conditions can affect the amount of hydrogen production (Stevens and McKinley, 1995, 2000; Anderson et al., 1998). These factors include water/rock ratio, fluid chemistry, pH, temperature, silica activity, surface passivation, mineral surface area, composition of the reaction vessel, and Fe(II/III) partitioning into secondary mineral phases (Béarat et al., 2006; Frost and Beard, 2007; McCollom and Bach, 2009; Klein et al., 2009; Mayhew et al., 2013; Andreani et al., 2013). Challenges arise from the fact that reactions are oftentimes conducted in silica serum vials with butyl stoppers that generate small amounts of hydrogen (Anderson et al., 1998; Mayhew et al., 2013; McCollom and Donaldson, 2016). Additionally, incomplete serpentinization of starting material and slow reaction rates make it difficult to judge the true

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