

**GENERATION OF HYDROGEN AND METHANE DURING LOW TEMPERATURE OLIVINE-WATER REACTIONS.** C. Donaldson<sup>1</sup> and T. M. McCollom<sup>1</sup>, <sup>1</sup>Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder CO 80309, USA (mccollom@lasp.colorado.edu).

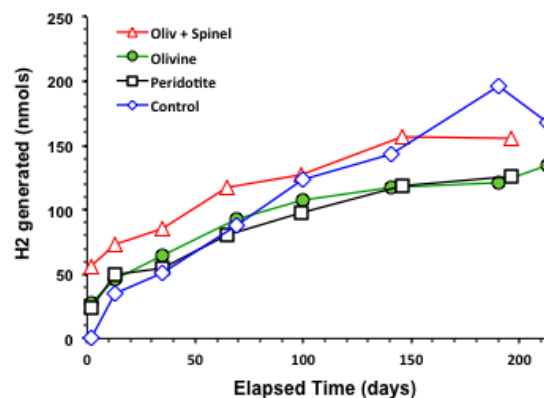
**Introduction:** The serpentinization of ultramafic rocks is widely recognized as a source of H<sub>2</sub> and CH<sub>4</sub> that supports chemolithoautotrophic microorganisms in settings such as deep-sea hydrothermal vents, alkaline springs, and the deep subsurface. In an effort to understand production of these volatiles in near-surface serpentinizing environments, a number of recent experimental studies have examined formation of H<sub>2</sub> and CH<sub>4</sub> during low temperature ( $\leq 100^\circ\text{C}$ ) fluid-rock interactions with olivine and ultramafic rocks [e.g., 1-5]. However, these studies have produced widely divergent estimates of H<sub>2</sub> and CH<sub>4</sub> production, and in many cases the results are inconsistent with higher temperature studies. In an effort to resolve these discrepancies, we performed a new set of experiments with carefully prepared substrates and controls to monitor contributions of H<sub>2</sub> and CH<sub>4</sub> from background sources. In addition, Mayhew et al. [2] had suggested that spinels may facilitate production of H<sub>2</sub> during serpentinization by promoting transfer of electrons, and we sought to test this proposition. To allow direct comparison with previous results, the experimental procedures were designed to parallel those used in other low temperature studies [2-5].

**Methods:** Experiments were conducted by heating minerals with sulfate-free artificial seawater at 90°C for 6-9 months, and periodically analyzing the headspace for H<sub>2</sub> and CH<sub>4</sub>. The experiments were performed in borosilicate glass bottles with butyl rubber stoppers that had been boiled in 1 M NaOH prior to use. The headspace of the bottles contained either N<sub>2</sub> or N<sub>2</sub> plus CO<sub>2</sub>. Reactant minerals were hand-picked for purity, ground, and wet sieved to a uniform grain size (53-212  $\mu\text{m}$ ). To examine the possible role of different substrates in H<sub>2</sub> and CH<sub>4</sub> production, several sets of experiments were performed with different reactants: 1) 99.9% pure olivine, 2) olivine w/MgAl-rich spinel, 3) olivine w/chromite, 4) olivine w/3 $\times$  chromite, 5) 2 $\times$ -olivine w/chromite, 6) chromite only, 7) harzburgite, 8) olivine w/CO<sub>2</sub>, 9) harzburgite w/CO<sub>2</sub>, and 10) harzburgite w/chromite+CO<sub>2</sub>. All experiments were run in triplicate.

**Results:** Each set of experiments exhibited a small, steady increase in H<sub>2</sub> over time (see Figure). However, in all cases, the amounts of H<sub>2</sub> produced were essentially identical to levels observed in control experiments that contained no minerals. Similarly, CH<sub>4</sub> was observed in small amounts that increased steadily in all

experiments, but again levels were nearly identical to controls. Inclusion of CO<sub>2</sub> in the headspace did not result in a detectable increase in CH<sub>4</sub> production. Inspection of olivine and pyroxenes with SEM after the experiments revealed no clear evidence of dissolution or surface alteration. A flaky, translucent precipitate formed in all experiments that lacked CO<sub>2</sub>, and was most readily apparent in the control and chromite-only experiments. EDS and XRD analysis indicated this phase was a Mg-bearing phyllosilicate, but its exact identity has not yet been determined. Because this phase occurred even in experiments without any silicate reactants, dissolution of the glass bottles was apparently the source of Si for these precipitates.

**Conclusions:** Contrary to previous experiments, we found no evidence for production of H<sub>2</sub> or CH<sub>4</sub> above background levels during low temperature reaction of olivine or harzburgite with water. In addition, we found no evidence that spinels stimulated the production of H<sub>2</sub> as previously proposed [2]. Overall, our results indicate that production of H<sub>2</sub> and CH<sub>4</sub> in low temperature serpentinizing systems is much more limited and occurs much more slowly than previous studies have suggested.



**References:** [1] Stevens T. O. & McKinley J. P. *Environ. Sci. Technol.*, 34, 826-831. [2] Mayhew L. E. et al. (2013) *Nat. Geosci.*, 6, 478-484. [3] Neubeck A. et al. (2011) *Geochem. Trans.*, 12:6. [4] Neubeck A. et al. (2014) *Planet. Space Sci.*, 96, 51-61. [5] Okland I. et al. (2014) *Chem. Geol.*, 387, 22-34.