CONSTRAINTS ON THE GENERATION OF HYDROGEN FOR MICROBIAL METABOLISM DURING SERPENTINIZATION. T. M. McCollom[1], W. Bach[2] and T. Hoehler[3], [1]CU Center for Astrobiology & Laboratory for Atmospheric and Space Physics, CB392, University of Colorado, Boulder, 80309, email: mccollom@lasp.colorado.edu. [2]Department of Geosciences, University of Bremen, 28334 Bremen, Germany. [3]NASA Ames Research Center, Moffett Field, CA.

Introduction: Serpentinization of ultramafic rocks generates fluids that are highly enriched in H_2 and CH_4 [1,2]. At sites where fluids are discharged from serpentinites at deep-sea hydrothermal vents or terrestrial springs, the fluids have been found to support communities of chemosynthetic microorganisms that utilize the H_2 and CH_4 for metabolic energy [1,3-6]. There is also isotopic evidence that chemosynthetic microbial communities may be active in the subsurface within serpentinites [7,8], but the microbiology of that environment has so far gone almost completely unexplored. Because many of the organisms present in these communities can exist independent of photosynthetic inputs, serpentinite-hosted systems have been proposed as analogs of habitable environments on the early Earth and on Mars [9-11].

In many cases, the amount of biological productivity that a particular environment can support will likely depend on the balance between the amount of energy supplied by the environment and the energetic demands of the organisms that might live there [12,13]. The capacity for serpentinites to provide metabolic energy sources to support microbial communities depends largely on the amount and rate of H_2 generated during the serpentinization process. At the present time, however, the factors that control H_2 generation during serpentinization remain poorly understood. Nevertheless, knowledge of how these factors influence H_2 production will be necessary to make quantitative assessments of the potential for serpentinites to support H_2-based microbial communities. The present contribution discusses some of the potential constraints on H_2 generation during serpentinization, and considers the implications of these constraints on the productivity of chemosynthetic microbial communities.

Thermodynamic constraints on hydrogen generation: Serpentinization can be represented by the general reaction: olivine + H_2O → serpentine + brucite + magnetite + H_2. Production of H_2 occurs as Fe(II) from olivine is oxidized by water to Fe(III), which principally winds up in magnetite. The actual stoichiometry of the reaction, and consequently how much H_2 is generated as a reaction product, depends on how the Fe(II) from olivine is partitioned among the product minerals. In particular, any Fe(II) that is incorporated into the serpentine and brucite without being oxidized will decrease the amount of H_2 generated. Recent thermodynamic models [14] indicate that temperature may exert an especially strong influence on the amount of Fe incorporated into brucite, with lower temperatures favoring brucite that is increasingly enriched in Fe. Fe-rich brucite has been reported in many serpentinites, but the factors controlling its formation have not been understood. It is likely that other factors such as fluid:rock ratio and bulk rock composition will also contribute to variations in Fe distribution in both serpentine and brucite, although these factors appear to have less impact than temperature. Overall, it is apparent that thermodynamic factors affecting Fe partitioning will contribute to large variations in H_2 generation as serpentinization proceeds under different conditions.

Kinetic constraints on serpentinization: In addition to thermodynamic factors, kinetic constraints on reaction rates will have a strong influence on the amounts and rates of H_2 production as serpentinization proceeds. Experimental studies of serpentinization indicate that the reaction is strongly temperature dependent, so that reaction rates become extremely sluggish at temperatures below ~150°C [15]. However, very few experimental studies of serpentinization have monitored H_2 production, and most of these have been performed at temperatures well above those inhabitable by microorganisms [16-19]. Nevertheless, the available data indicate that H_2 production drops off steeply at lower temperatures (Fig. 1). It is likely that this decrease reflects the combined effects of slow reaction kinetics and increased partitioning of Fe(II) into brucite.

Implications for biological systems: At high temperatures (~200°C and above), serpentinization proceeds rapidly and thermodynamic factors favor formation of magnetite relative to Fe-rich brucite and serpentine. As a consequence, hydrothermal fluids formed at these temperatures are highly enriched in H_2 that can support prolific biological communities [refs]. Thermodynamic models [14] predict that maximum H_2 concentrations in hydrothermal fluids should be produced during serpentinization at temperatures around 300°C. Since all serpentinite-hosted hydrothermal systems that have been identified to date occur at temperatures much above or below this

apparent optimum, it is possible that serpentinite-hosted environments may exist that are even more productive than those presently recognized.

At lower temperatures, sluggish reaction kinetics and increased partitioning of Fe into brucite may severely limit the amount of H_2 generated. Indeed, the rates of H_2 generation at temperatures below about 100°C may become so slow that the reaction is unable to supply sufficient H_2 to meet the energetic demands of microorganisms, limiting the habitability of these environments [see Hoehler et al. abstract, this meeting]. In any case, lower temperature serpentinization environments are likely to be able to support significantly less microbial activity than those fed by higher temperature systems.

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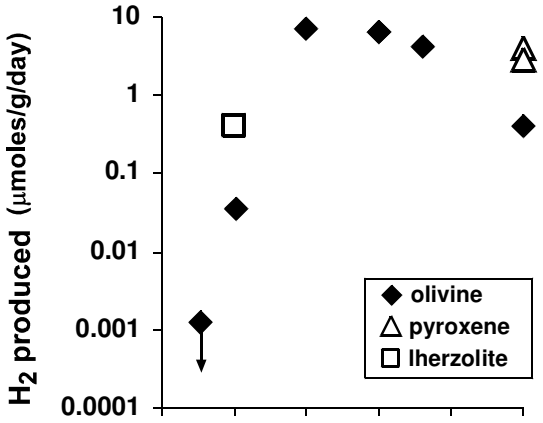

Figure 1. Summary of all currently available experimental data for rates of hydrogen generation during serpentinization of ultramafic rocks and their primary constituent minerals olivine and pyroxene. Data derived from experimental results reported in refs. 16-19 and unpublished results of the authors.