EXPERIMENTAL CONSTRAINTS ON RATES OF HYDROGEN AND METHANE GENERATION IN SERPENTINIZING ENVIRONMENTS. T. M. McCollom,* Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO 80309-0600, mccollom@lasp.colorado.edu.

Introduction: The capacity for serpentinizing systems to support chemolithoautotrophic microbial communities is largely dependent on the rates and amounts of molecular hydrogen (H₂) and methane (CH₄) generated during the process of serpentinization. In recent years, numerous laboratory experimental studies have been conducted that focus on the formation of these compounds in an effort to better understand the processes involved. This presentation will provide an overview of these studies and examine implications for the capacity of serpentinizing environments to support life.

Rates of serpentinization: The overall rate of serpentinization exerts a large influence on the rates of H₂ and CH₄ generation. Experimental studies conducted in the 1970s and 1980s had suggested that serpentinization proceeds very rapidly on geological timescales. More recent studies, however, indicate that reaction rates for serpentinization are 50-80 times slower than the older studies had indicated [1,2]. These newer rate estimates suggest, for example, that complete serpentinization of peridotites in shallow subaerial settings would require several hundred thousand years or more to go to completion, rather than the few thousands of years implied by older studies.

Hydrogen generation: Over the last couple of decades, a number of experimental studies have monitored H₂ production during fluid:rock interaction with ultramafic minerals. These studies encompass temperatures ranging from 25 to 400 °C and several different rock/mineral substrates (e.g., pure olivine, harzburgite, lherzolite). A compilation of H₂ generation rates from these studies shows widely ranging values, with rates spanning several orders of magnitude at comparable temperatures. To some extent, variations in H₂ generation rates among these studies can be explained by differences in experimental design, such as grain size, presence or absence of headspace, etc. However, these design differences likely account for only a relatively small fraction of the variation, and a complete explanation for the full range of rates remains undetermined.

At low temperatures (<100 °C), reported H₂ generation rates span more than four orders of magnitude, and the rates of production in several studies exceed those reported at much higher temperatures. Extrapolation from higher temperature studies indicate that lower reported rates are probably more reasonable, but the cause of the anomalously high rates reported in some studies is unclear. If the lower rates are representative, it implies that fluid residence times of many hundreds of years or more may be required to explain the H₂ concentrations observed in low temperature subaerial serpentinite settings.

Methane generation: There is considerable evidence that CH₄ formed by abiotic processes is present in many natural serpentinites. However, because biological, thermogenic, and magmatic sources also contribute to CH₄ in serpentinizing environments, the exact amount of abiotic CH₄ present in many systems remains uncertain. This uncertainty is particularly acute in low temperature continental serpentinites, where methanogenic organisms have been shown to be present.

As with H₂, the last couple of decades have seen publication of numerous experimental studies that investigated abiotic synthesis of CH₄ during fluid:rock interactions at conditions relevant to serpentinizing environments. These studies, however, have reported strongly conflicting results, with some finding strong kinetic inhibitions to CH₄ synthesis even at temperatures as high as 300-400 °C, while others claim synthesis at much lower temperatures (25-200 °C). A couple of recent studies performed in my lab attempted to resolve this discrepancy [3,4], and the results indicate that the CH₄ observed in experiments conducted at low temperatures (<300 °C) is most likely derived from background sources rather than from reduction of inorganic carbon. Overall, the experimental results indicate that abiotic conversion of dissolved inorganic carbon to CH₄ will be extremely sluggish in shallow, lower-temperature serpentinizing systems unless specific catalysts are present to promote the reaction.

Implications for natural systems: The available experimental data indicate that serpentinization as well as the generation of H₂ and CH₄ are very sluggish at temperatures <100 °C. For this reason, it appears unlikely that the elevated H₂ and CH₄ concentrations observed in many subaerial serpentinites can be accounted for by reaction of shallow groundwater having short residence times. Instead, these compounds probably reflect input from deeper fluid sources with longer residence time and/or higher temperatures.