HYDROGEN AND METHANE GENERATION IN SERPENTINIZING SYSTEMS: AN EXPERIMENTAL PERSPECTIVE. T. M. McCollom¹ and F. Klein², ¹Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO 80309 (mccollom@lasp.colorado.edu) and ²Woods Hole Oceanographic Institution, Woods Hole, MA.

Introduction: Serpentinization is widespread on the terrestrial seafloor as seawater circulates through, and reacts with, the ultramafic rocks that constitute a significant fraction of the ocean lithosphere. Fluids discharged from serpentinizing rocks are often highly enriched in molecular hydrogen (H₂) and methane (CH₄), both of which provide sources of metabolic energy to support autotrophic microbial communities when the fluids mix with oxidized seawater at the seafloor [1,2]. Given the predominance of ultramafic rocks in solid bodies in the solar system, it is likely that serpentinization has occurred, and may be ongoing, in the rocky mantles underlying the oceans of icy satellites [3,4,5]. In these bodies, serpentinization has the potential to support microbial ecosystems similar to those found on the terrestrial seafloor.

Although serpentinization on Earth has been widely studied in field and laboratory settings, many aspects of this deceptively complicated process remain poorly understood. In particular, the rates of overall reaction, amounts and rates of hydrogen production, and the source of methane remain matters of significant uncertainty and debate. We will summarize some of our latest experimental studies that examine these issues.

Results: Results of recent experimental studies indicate that rates of serpentinization are substantially slower than older studies had indicated [6,7,8], although interpretation of these rates is complicated by results from other studies that indicate substantially higher rates under some experimental conditions [9,10]. Experimental results also indicate that rates decrease sharply with lower temperatures, suggesting that the process is extremely sluggish on geologic timescales at temperatures below ~100 °C or so [7]. Rates of H₂ production also fall off steeply with decreasing temperature, both due to slower overall reaction rates and increased partitioning of ferrous Fe (Fe^{II}) from the ultramafic precursors into serpentine and brucite rather than producing the ferric Fe (Fe^{III}) that leads to H₂ production. Together, these results suggest that fluids circulating through ultramafic rocks at temperatures below ~100 °C are unlikely to produce significant amounts of serpentinization or generate much H₂ unless they are present in the rocks for millions of years.

Recent experimental studies of the abiotic production of CH₄ from dissolved CO₂ also provide further confirmation that this process is extremely sluggish at

temperatures below ~ 300 °C [11,12], indicating that reduction of dissolved inorganic carbon in circulating seawater is unlikely to account for the CH₄ observed in lower temperature serpentinizing fluids. Instead, the source of these compounds may be higher temperature reactions occurring deeper in the system. These experimental results are consistent with recent results from natural systems that indicate the CH₄ in seafloor hydrothermal fluids has a high-temperature origin, possibly involving reduction of mantle-derived CO₂ deep within the system [13,14].

Implications for icy worlds: The experimental studies indicate that serpentinization of ultramafic rocks in the rocky mantles of icy satellites can provide a source of H₂ and CH₄ to the oceans, but may require elevated temperatures or very long residence times to attain significant levels of these compounds in the fluid. If the overlying oceans contain electron acceptors such as O₂ or SO₄²⁻, venting fluids would be capable of supplying the same kinds of metabolic energy that supports autotrophic microbial communities in terrestrial systems [15].

References: [1] Schrenk M. O., et al. (2013) Rev. Mineral. Geochem. 75, 575-606. [2] McCollom T. M. and Seewald J. S. (2013) Elements 9, 129-134. [3] Hsu H.-W. et al. (2015) Nature 519, 207-210. [4] Waite J. H. et al. (2017) Science 356, 155-159. [5] Vance S. et al. (2007) Astrobiology 7, 987-1005. [6] Malvoisin B. et al. (2012) JGR 117, B04102. [7] McCollom T. M. et al. (2016) GCA 181, 175-200. [8] McCollom T. M. et al. submitted to GCA. [9] Andreani M. et al. (2013) Am. Mineral. 98, 1738-1744. [10] Lafay R. et al. (2012) J. Crystal Growth 347, 62-72. [11] McCollom T. M. (2016) PNAS 113, 13965-13970. [12] McCollom T. M. and Donaldson C. (2016) Astrobiology 16, 389-406. [13] McDermott J. M. et al. (2015) PNAS 112, 7668-7672. [14] Wang D. T. et al. (2018) GCA 223, 141-158. [15] McCollom T. M. (2007) Astrobiology 7, 933-950.