Clumped isotope signatures of serpentinization-associated methane from the Philippines

KRISTIN WOYCHEESE[1]*, D'ARCY MEYER-DOMBARD[2], DAWN CARDACE[3], CARLO A. ARCILLA[4], SHUHEI ONO[1]

[1]Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, USA. *kristinw@mit.edu

[2]Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, IL, USA.

[3]Department of Geosciences, University of Rhode Island, Kingston, RI, USA.

[4]National Institute of Geological Sciences, University of the Philippines, Diliman, Quezon City, Philippines.

Serpentinization is a metamorphic process that yields serpentine, brucite, and magnetite from the dissolution of olivine. Hydrogen and methane gas are also produced, resulting in ultrabasic (pH > 10), Ca^{2+}-rich fluids. In the deep subsurface, these conditions fuel microbial food webs that are decoupled from the products of photosynthesis. Throughout the Solar System, the same process may help craft habitable environments on rocky bodies such as Mars or Europa.

Methane is thought to arise abiotically during serpentinization by Fisher-Tropsch-type reduction of CO_2, but thermo- and biogenesis cannot be ruled out [1]. Stable isotopic analysis of δD from methane-rich gas seeps in the Philippines demonstrated equilibration temperatures of 110-125°C, indicative of abiogenic methane production with possible thermogenic mixing [2]. Recently, hydrogenotrophic methanogens were detected in serpentinizing fluid from the Philippines [3] and bioenergetic models suggest that methanogenesis may be favorable in these environments [4].

Here we present the first study of methane clumped isotope ($^{13}CH_3D$) signatures from the Philippines to identify any biogenic signature in serpentinization-associated springs and seeps. Using tunable infrared laser direct absorption spectroscopy (TILDAS), we identify the ratio of methane clumped isotopes to constrain the temperature of equilibration in the system. Coupled with metagenomic analysis of serpentinizing fluids, we evaluate the plausibility of a biogenic component to the clumped isotopic signature of serpentinization-associated methane in the Philippines.

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