ORIGIN OF ABIOTIC METHANE IN SUBMARINE HYDROTHERMAL SYSTEMS. J. S. Seewald[1], C.R. German[1], N. G. Grozeva[1], F. Klein[1], J. M. McDermott[2], S. Ono[3], E. P. Reeves[4], , D. T. Wang[5] [1]Woods Hole Oceanographic Institution, Woods Hole, MA 02543, jseewald@whoi.edu, [2]Lehigh University, Bethlehem, PA 18015, [3]Massachusetts Institute of Technology, Cambridge, MA 02139, [4]University of Bergen, Bergen N-5020, Norway, [5]ExxonMobil, 22777 Springwoods Village Parkway, Spring, TX 77389.

The origin of CH_4 in hydrothermal systems on Earth and other ocean worlds has received significant attention, due to the central role of abiotic organic synthesis in models for the hydrothermal origin of life. In addition, metabolic pathways that consume or produce CH_4 represent sources of energy supporting primary-producing microorganisms in complex vent ecosystems. Models for the formation of abiotic CH_4 and other hydrocarbons observed in vent fluids involve reduction of ΣCO_2 and/or CO through Fischer–Tropsch-type processes during active circulation of seawater-derived hydrothermal fluids that are enriched in dissolved H_2 due to serpentinization of host rocks. Others have suggested that leaching of CH_4 and low-molecular weight hydrocarbons from magmatic fluid inclusions hosted in plutonic rocks may contribute to the inventory of organic compounds in hydrothermal vent fluids.

In recent years we have examined the chemical and isotopic composition of actively venting submarine hydrothermal fluids and volatile species trapped in fluid inclusions in plutonic rocks to assess chemical processes that regulate the formation of CH_4. Vent fluids from the Von Damm vent field at Mid-Cayman spreading center, for example, contain radiocarbon dead dissolved CH_4 that, based on its stable carbon isotopic composition cannot be derived by reduction of radiocarbon-bearing CO_2 during convective circulation of seawater-derived vent fluids[1]. The data suggest that fluid-rock interaction during hydrothermal circulation releases pre-existing CH_4 from fluid inclusions hosted in plutonic rocks. The similarity in isotopic data and C_1/C_{2+} molal concentration values across multiple vent fields globally, suggests that processes responsible for CH_4 generation at Von Damm are also occurring at the other unsedimented sites.

Clumped isotopologue analysis of dissolved CH_4 from four geochemically-distinct hydrothermal vent fields (including Von Damm and Lost City) yields apparent equilibrium temperatures that average 310 °C, with no apparent relation to the wide range of measured fluid temperatures (96–370 °C) and chemical compositions[2]. Combined with very similar bulk stable isotope ratios ($^{13}C/^{12}C$ and D/H) of methane across the suite of hydrothermal fluids, all available geochemical and isotopic data suggest a common mechanism of methane generation at depth that is disconnected from active fluid circulation. Leaching of pre-existing CH_4 hosted in fluid inclusions can account for the uniformity of formation temperatures indicated for CH_4 across multiple vent fields.

Mineralogical, chemical, and isotopic examination of fluid inclusions in olivine-rich basement rocks from active serpentinization systems and an ophiolite provide evidence for the presence of abundant CH_4-rich secondary fluid inclusions hosted in olivine[3]. Measurements of stable carbon isotopic compositions of CH_4 and ethane released from fluid inclusions indicate a range of compositions that are similar to the range of isotopic compositions observed for these species in ultramafic-influenced mid-ocean ridge vent fluids. Values of C_1/C_{2+} molal ratios in fluid inclusions are lower than values for hydrothermal vent fluids, suggesting that longer chain hydrocarbons may be degrading once released from fluid inclusions to high-temperature seawater-derived hydrothermal fluids.

Collectively, our results are consistent with a model where magmatic CO_2 is trapped in secondary inclusions. Serpentinization reactions within fluid inclusions generate H_2 that results in the reduction of CO_2 to form CH_4 and lesser quantities of C_{2+} alkanes via Fischer-Tropsch-type reactions. The hydrocarbons are released to seawater-derived hydrothermal fluids that vent at the seafloor during convective circulation through the oceanic lithosphere. Formation of CH_4 during water-rock reactions at temperatures lower than 200 °C or during the convective circulation of hydrothermal fluids does not appear to contribute significant quantities of CH_4 to mid-ocean ridge hot springs. These observations can be used to not only assess the kinetics and environments conducive to abiotic CH_4 formation, but also the likelihood CH_4 may fuel chemosynthetic-based life in ocean worlds beyond Earth.

References: [1] McDermott J.M., Seewald J.S., German C.R., and Sylva S.P. (2015) Proc. Nat. Acad. Sci. 112, 7668-7672. [2] Wang D.T, Reeves E.P, McDermott J.M, Seewald J.S., and Ono S. (2017) Geochim. Cosmochim. Acta 223, 141-158. [3] Grozeva N. G. (2017) unpublished Ph.D. Thesis, Woods Hole Oceanographic Insitution.