Novel isotopic techniques to investigate the deep subsurface acetate cycle

ELLIOTT P. MUELLER1, JULIANN PANEHAL1, CHRISTIAN T. HANSEN2, MIN SONG3, JASON BOETTGER4, VERENA B. HEUER5, OLIVER WARR3, WOLFGANG BACH2, KAI-UWE HINRICHS2, JOHN EILER1, VICTORIA ORPHAN1, BARBARA SHERWOOD LOLLAR3 AND ALEX L. SESSIONS1

1California Institute of Technology
2MARUM, University of Bremen
3University of Toronto
4University of Texas at El Paso
5MARUM – Center for Marine Environmental Sciences, Faculty of the University of Bremen

Presenting Author: emueller@caltech.edu

Deep groundwater sequestered in the continental crust represents a vast, under-constrained reservoir of water and carbon. These environments host microbial communities that can be isolated from surficial biogeochemical cycles on timescales from decades to hundreds-of-millions of years [1]. Carbon cycling in subsurface fracture fluids operates on a spectrum from abiotically- to biotically-driven. Organic acids may play an important role across this spectrum, as they can be synthesized by microbial metabolisms or via water-rock interactions, including radiolytic chemistry. They can also accumulate to low-millimolar concentrations in the subsurface [2]. Here, we applied a new Orbitrap-based technique [3] for measuring d13C and d2H of acetate to investigate organic acid turnover in an abiotically dominated site (Kidd Creek Mine, Canada) and a more microbially active site (Birchtree Mine, Canada). We measured d13C values of acetate that were relatively enriched in Kidd Creek fracture fluids (-7 to -9‰) and relatively depleted in Birchtree (-27‰), potentially reflecting different formation mechanisms [2]. However, at both sites, we determined that the hydrogen atoms on acetate’s methyl group were in isotopic disequilibrium with ambient water, based on theoretical calculations of the acetate-water equilibrium isotope effect (EIE). Through a series of high-temperature hydrothermal autoclave experiments (100-250°C, 30 MPa), we demonstrated that acetate exchanges hydrogen atoms with water at a temperature-dependent rate. Given Kidd Creek’s in situ temperature (25°C), its pool of acetate should have fully equilibrated with fracture fluids within 10⁶ years. If the calculated EIE is accurate, acetate could be cycling 1000-times faster than the residence time of Kidd Creek’s fluids (10⁸-10⁹ years). Our observations may suggest that radiolytic reactions between host rock and deep groundwater sustain long-term organic acid production. Organic acids are common substrates for microorganisms to assimilate carbon and generate energy. Therefore, a sustainable, low-temperature source of acetate that only requires water-rock interactions represents an auspicious mechanism to support early-life on Earth and microbial life on other celestial bodies.