Abiogenic and microbial cycling of volatile fatty acids in ancient crustal fracture waters in the Canadian Shield

J. M. MCDERMOTT[*1], V. B. HEUER[2], S. TILLE[1], J. J. MORAN[3], G. F. SLATER[3], C. N. SUTCLIFFE[1], C. R. GLEIN[1], K.-UWE HINRICHS[2] AND B. SHERWOOD LOLLAR[1]

[1]Earth Sciences, University of Toronto, Toronto, ON, Canada ([*]jill.mcdermott@utoronto.ca)
[2]MARUM, University of Bremen, Germany
[3]Geography and Earth Sciences, McMaster University, Canada

Fracture waters within the Precambrian Shield rocks of Canada and South Africa have been sequestered underground over geologic timescales up to 1.5 Ga [1] [2]. Tapped by deep mines, these fluids have been shown to host a low-biomass, low-diversity microbial ecosystem at some sites [2]. The question of whether abiogenic or biogenic geochemical processes dominate in deep, isolated aqueous subsurface environments has important implications for habitability, and for the role played by abiotic organic synthesis in carbon flux from the deep to the surface biosphere.

Volatile fatty acids (VFAs) may support chemosynthetic communities, e.g. in terrestrial [3] and deep-sea [4] hot springs. We present abundance and $\delta^{13}C$ analysis for VFAs in a spectrum of Canadian Shield fluids characterized by near-neutral pH and highly variable H_2, CH_4, C_{2+} *n*-alkane, and SO_4 contents. Isotope mass balance indicates that elevated levels of acetate (371-816 μM) may be generated by microbial fermentation in Birchtree mine. In contrast, thermodynamic considerations and isotopic signatures of the notably higher acetate (1.31-1.91 mM), as well as formate and propionate abundances (371-816 μM and 200-379 μM, respectively) found at Kidd Creek suggest possible abiogenic production via reduction of dissolved inorganic carbon with H_2 for formate, and inorganic oxidation of C_{2+} *n*-alkanes for acetate and propionate. VFAs dominate the pool of dissolved and total organic carbon in the mines surveyed, and as such represent a potential key substrate for life.

[1] Holland *et al*. (2013) *Nature* **497**: 367-360. [2] Lin *et al*. (2006) *Science* **314**: 479-482. [3] Windman *et al*. (2007) Astrobiology **7** (6): 873-890. [4] Lang et al. (2010) Geochim. Cosmochim. Acta **92**: 82-99.