On organic synthesis reactions driven by serpentinization

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Moderate temperature, alkaline fluids with high amounts of hydrogen and methane issue from the seafloor in oceanic core complexes [1]. These fluids contain low molecular weight organic molecules likely related to abiotic synthesis [2,3]. The amount of dihydrogen produced during serpentinization of mantle peridotite at elevated temperatures is the driver behind forming abiotic organic carbon species. Recent models of serpentinization [e.g., 4, 5] provide insights into the quantity of hydrogen which is produced at different temperatures and water-rock-ratios from variable lithologies. Based on these models, affinites for the synthesis of organic molecules during the serpentinization process were calculated.

Methane is predicted to be the dominate organic species, but its formation is known to be kinetically sluggish [6]. Preliminary results for different serpentinization scenarios show strong affinities in the overall reaction for hydrocarbons at low temperatures. These reactions are kinetically sluggish in aqueous solutions at low temperatures, and at higher temperatures, when rates are increased, the affinities decrease because less hydrogen is available from fluid-rock equilibrium. When the affinities of the overall reactions are normalized to electrons transferred, the highest affinities are predicted for formic acid, which is indeed elevated in fluids from the Lost City vent field [3].

Mixing of 350°C hydrothermal fluid from serpentinization systems with cold seawater also creates abundant driving force for organic synthesis [7]. As the time scales of mixing much exceed those at which abiotic organic synthesis reactions proceed, these environments generate an energetically feasible habitat for microbes. Affinity calculations for these environments allow an assessment of energy availability for catabolism, which can be coupled to anabolic energy demand to characterize the uniqueness of serpentinization systems.

[1] Kelley et al. (2001) Nature **412**, 145. [2] Proskurowski et al. (2008) Science **319**, 604. [3] Lang et al. (2010) GCA **74**, 941. [4] McCollom and Bach (2009) GCA **73**, 856. [5] Klein et al. (2009) GCA **73**, 22, 6868. [6] Seewald et al. (2006) GCA **70**, 446. [7] Shock and Schulte (1998) J. Geophys. Res. **103**, 28513.

Subsurface biogeochemistry of hydrothermal flow at the Hook Ridge, Bransfield Strait

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Metalliferous sediments at active hydrothermal vent sites host significant populations of free-living and symbiotic chemosynthetic microorganisms associated with benthic fauna. Reduced hydrothermal fluids flow through the sediments and interact with oxic, overlying seawater to create steep redox gradients in the subsurface biosphere. The products of these redox reactions provide a suite of electron donors and acceptors that stimulate microbial metabolism and support chemosynthetic consortia of subseafloor microorganisms. We are yet to fully understand the impact of macro-faunal and microbial communities on the geochemical flux of C, S, Fe, Mn and other elements across redox boundaries near the sediment-water interface. Here we present the pore-fluid and solid phase geochemistry of sediments from Hook Ridge - an extensive, high-temperature, hydrothermal system in the central Bransfield Strait, Antarctica [1].

Hook Ridge hydrothermalism is characterised by areas of shimmering water and water column $E_{\rm h}$ anomalies at a depth of 1100m. Ship-board and shore-based, analyses of extracted pore-fluids demonstrate the advection of low-chlorinity (<490 mM), high-sulfide (>120 μ M), high-methane (>15 μ M) and Fe-rich (>545 μ M) fluids through the sediments, at rates of 20-50 cmyr $^{-1}$. Downcore sulfate-methane distributions suggest the presence of anaerobic oxidation of methane (AOM) at this site. These sediments are dominated by patches of the siboglinid chemosynthetic polychaete *Sclerolinum sp.* that likely contain sulfophilic chemosynthetic symbionts [2]. Faunal, mineralogical and geochemical analyses of Hook Ridge sediments are used to constrain the distribution and impact of the biogeochemical processes occurring in this sediment-hosted hydrothermal system.

[1] Klinkhammer *et al.* (2001) *EPSL* **193**, 395-407. [2] Sahling *et al.* (2005) *Limnol. Oceanogr.* **50**, 598-606.