

THE ENERGETICS OF CARBON COMPOUND REDOX CHEMISTRY IN SERPENTINIZING FLUIDS.

K. J. Robinson¹ and E. L. Shock^{1,2}, ¹Department of Chemistry and Biochemistry, ²School of Earth and Space Exploration, Arizona State University.

Introduction: Serpentinization of ultramafic rock produces hyperalkaline reducing aqueous conditions. Reduction of inorganic carbon to organic carbon in natural serpentinizing settings has been inferred by analyzing input and output fluids [1-12], but it is still unknown where in the system or at what stage of reaction progress this reduction takes place. Carbon reduction has been demonstrated in serpentinization experiments [13-22], allowing attention to shift to reaction mechanisms, including whether organic compounds form reversibly or irreversibly with respect to one another and inorganic carbon species [16,18], and how product formation depends on the order of reaction intermediates. As a consequence it will become possible to establish the degree to which processes of carbon reduction are abiotically or biologically mediated in lower temperature serpentinizing systems [23].

Field Sampling: Water samples were collected from the Samail Ophiolite in the Sultanate of Oman from shallow groundwater (system input) and hyperalkaline seeps (system output) and analyzed for dissolved concentrations of inorganic carbon (with $\delta^{13}\text{C}$), organic carbon (with $\delta^{13}\text{C}$), formate, acetate, hydrogen (H_2), methane (CH_4), and ethane. The results of this survey indeed show that dissolved inorganic carbon, present in groundwater input, is largely removed from serpentinized fluid output. Instead, serpentinized fluid output contains significant increases in the individual organic compound species mentioned above relative to groundwater input. A geochemical suite of analyses was also performed at these sample sites, which included measurements of dissolved major anions, major cations, and trace metals.

Equilibrium Calculations: To better characterize individual organic compound formation with respect to surface and subsurface conditions, the above organic compound and geochemical data were subjected to thermodynamic analyses. Calculations were performed to assess whether individual organic compounds were in equilibrium with one another or in equilibrium with inorganic carbon in serpentinized fluids. For organics far from equilibrium in surface samples temperature, pressure, and composition conditions were identified that satisfied equilibrium conditions in the subsurface.

Based on these calculations, acetate is in apparent equilibrium with inorganic carbon and H_2 in low temperature surface samples. Thermodynamic analysis of formate suggests that formate last equilibrated in a low temperature part of the system with greater H_2 abun-

dance, higher pressure, and lower pH; this might describe a deeper part of the serpentinizing system or earlier stage of reaction progress. Methane equilibrium with inorganic carbon and H_2 is satisfied either at much higher temperatures or in a low temperature inorganic carbon-limited part of the system; ethane equilibrium follows a similar pattern.

Bioenergetic Calculations: Calculations were also performed to quantify the amount of redox energy available from biologically relevant reactions. For example, aerobic oxidation of organic compounds in these samples yields abundant energy for metabolism when the reaction products are inorganic carbon species. Aerobic oxidation of organic compounds is also highly favorable, though to a lesser extent, when the reaction products are more oxidized organic compounds relative to the reactants (CH_4 oxidized to formate: $\Delta_r G \approx -100 \text{ kJ/mol e}^-$), instead of inorganic carbon (CH_4 oxidized to CO_3^{2-} : $\Delta_r G \approx -175 \text{ kJ/mol e}^-$).

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