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Characterizing the Biotic Fringe in Hydrothermal Ecosystems

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Deep in the Earth's crust, where temperatures and pressures are high and where stable thermodynamic equilibrium is attained, the active processes are all abiotic. Somewhere toward the Earth's surface conditions become habitable. Temperatures and pressures are still high, but not so high that stable equilibrium is reached rapidly. Disequilibrium states develop that contain sources of geochemical energy. Biochemical processes, which may be at their extreme limits, are capable of tapping into these geochemical energy sources and supporting extremely thermophilic micro-organisms. As a result, a transition occurs in this "biotic fringe" from abiotic geochemical processes characterized by water/rock reactions to biogeochemical processes that support hydrothermal ecosystems. Energy sources used by chemotrophic organisms are kinetically sluggish or inhibited oxidation-reduction reactions. The kinetic complexities of many of these reactions are familiar to geochemists and petrologists who study the formation of ore deposits, low-temperature hydrothermal alteration, and weathering. What constraints are supplied by the rates of oxidation-reduction reactions? Although rates of these processes have received minimal attention compared with rates of redox-insensitive mineral dissolution and precipitation reactions, practical experience in hydrothermal labs indicates that temperatures above 200 to 250 ºC are required for equilibration on laboratory time scales for many reactions involving iron and copper sulfides and oxides. Reactions involving iron silicates require higher temperatures as do those involving carbon oxide gases (see: Zolotov and Shock, 1999 for a review). As a comparison, at ideal growth conditions in the lab many thermophiles have doubling times of less than an hour, which means that they can rapidly take advantage of sources of chemical disequilibrium. Therefore, in dynamic geochemical systems with a steady supply of reactants at a nearly constant state of disequilibrium, it is plausible that biotically catalyzed redox processes occur faster than their abiotic analogues even at temperatures of 200 ºC and above. High-temperature oxidation reactions (in the presence of the atmosphere) tend to be rapid, while reduction reactions (even in the presence of hydrogen overpressures) are generally slower. Therefore, experience in the lab is consistent with the metabolisms of hyperthermophiles, many of which catalyze reduction reactions (sulfur reduction, methanogenesis, sulfate reduction) to gain metabolic energy. Although reactions involving iron oxides tend not to equilibrate below 300 ºC on the time scale of laboratory experiments involving aqueous solutions, they may equilibrate at lower temperatures in nature given longer spans of time. Nevertheless, there are known hyperthermophiles that either oxidize or reduce iron indicating that equilibrium is not reached at temperatures where they thrive. Therefore, a combination of observations, lab experience, and hyperthermophilic metabolism suggests that iron disequilibria persists at temperatures to at least 150 ºC. Hydrogen sulfide oxidation to sulfur is relatively rapid at high temperatures in contact with the atmosphere. Accordingly, no thermophilic organisms are known that make a living from this reaction. However, oxidation of hydrogen sulfide to sulfur coupled with nitrate reduction to nitrite or nitrogen is slow enough to support thermophiles. Similarly, the reduction of sulfur to hydrogen sulfide is kinetically inhibited, and a host of thermophiles and hyperthermophiles gain energy from sulfur reduction. Even more energy may be provided by heterotrophic sulfate reduction reactions depending on the organic composition of geochemical systems. In addition, heterotrophic and autotrophic methanogenesis reactions are thermodynamically favored but kinetically inhibited wherever there are accumulations of hydrocarbons and/or organic matter (Helgeson et al., 1993), suggesting that catalyzing methane production is another lucrative biogeochemical process at the biotic fringe.

Helgeson HC, Knox AM, Owens CE, Shock EL, *Geochim. Cosmochim. Acta*, **57**, 3295-3339, (1993).

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