# Hydrothermal ecosystems in a planetary context

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The phenomenal rates of biological productivity in submarine hydrothermal systems are driven by geochemical disequilibria between vent fluids and seawater, and are a direct consequence of reactions between seawater, basalt, and other rocks in the oceanic crust. Thermodynamic models of fluid mixing in submarine hydrothermal systems (McCollom and Shock, 1997) show that sources of inorganic geochemical energy at temperatures less than about 50°C are characterized by reactions such as the oxidation of methane and hydrogen sulphide. Methane oxidation is oxygen limited at temperatures greater than 33°C, and methane limited below 33°C. Sulphide oxidation is oxygen limited above about 4°C and hydrogen sulphide limited below. The energetics of these reactions, together with iron oxidation above 27°C, depend directly on a source of oxygen from photosynthesis at the surface.

In contrast, at higher temperatures, geochemical processes dictate that the inorganic energy sources for life are reductive reactions like methanogenesis and sulphur reduction. Hyperthermophilic chemolithoautotrophs that pursue these reactions do not require the products of photosynthetic organisms. At 100°C and 250 bar – prime hydrothermal habitat – autotrophic methanogens combine $CO_2$ (or bicarbonate) with $H_2$ from vent fluids to generate $CH_4$. This reaction yields 103.8 kJ per mole of $CH_4$ generated, and the metabolically-captured portion of this energy drives the biological processes of these organisms. Conditions conducive to methanogenesis are also conducive to organic synthesis. Generation of acetic acid from $CO_2$ and $H_2$ at 100°C yields 66.1 kJ $mol^{-1}$, if the background source of acetic acid is the average seawater value of 50 $\mu g\ l^{-1}$ (Shock *et al.*, 1998).

Geologic and geochemical support for life in hydrothermal ecosystems stands in stark contrast to photosynthesis in the atmosphere where thermodynamic work is required to make organic compounds in a strongly oxidizing environment. In submarine hydrothermal ecosystems methane is more stable than the mixture of hydrogen and carbon dioxide (or bicarbonate) resulting from fluid mixing, but so are many ketones, alcohols, carboxylic acids and other organic compounds (Shock and Schulte, 1998). Amino acid synthesis at 100°C in submarine hydrothermal ecosystems is exergonic for eleven of the twenty protein-forming amino acids (Amend and Shock, 1998). Perhaps it should come as no surprise that doubling times for hyperthermophiles can be less than 30 minutes, and overall rates of productivity in hydrothermal ecosystems are enormous (Lutz *et al.*, 1994).

Recognition that hydrothermal systems provide extremely conducive environments for life leads to hypotheses about the high-temperature emergence of living systems on the early Earth. Such hypotheses are corroborated by the fact that the phylogenetic tree, constructed from small subunits of RNA, indicates that hyperthermophiles populate the lowest branches. By inference, these organisms are closest (in an evolutionary sense) to the last common ancestor of the three domains of life. This fact has been used to argue that this common ancestor was also a hyperthermophile, and that life emerged on the Earth in water at elevated temperatures in settings like hot springs and hydrothermal systems (Pace, 1997). Some investigators contend that a hyperthermophilic common ancestor does not demand that high temperatures were required for the emergence of the first living system, and argue instead that organisms in seafloor hydrothermal systems may have been the only survivors of the last large impact during late-stage accretion of the Earth (Lazcano and Miller, 1994). Such arguments strive to preserve notions about the origin of life that predate plate tectonics, modern genetics, and planetary exploration, and seem to miss the point that the conditions in submarine hydrothermal systems are uniquely suited to the synthesis and preservation of organic compounds. It follows that hydrothermal systems may be similarly conducive to the emergence of life. As a consequence, hydrothermal systems are often put forth as likely habitats throughout the solar system.

The jovian moon Europa is emerging as a prime site of exobiological interest, especially as evidence for an ocean underneath its icy surface continues to accumulate (Carr *et al.*, 1998). Measurements of Europa's gravitational moments strongly suggest that

Europa has differentiated into an iron core, a rock mantle, and a thick (~150 km) surface water/ice layer (Anderson *et al.*, 1997). Hydrothermal systems are an inescapable consequence of volcanic activity in the presence of liquid water, and would have been abundant during heating, differentiation and cooling phases of Europa's evolution. After differentiation, compositions are likely to be basaltic in the parts of the rock mantle that would be in close proximity to the ice layer. If so, hydrothermal systems would have been hosted in basalt for the past ~3.5 b.y., including systems that might accompany present-day rock-mantle/ice-layer boundary volcanism driven by tidal forces (McKinnon and Shock, 1998). However, there is considerably more to hydrothermal habitats than hot water. Fluid and rock compositions have to be able to provide enough energy to drive metabolic processes, and geophysical and petrologic processes have to be able to generate those fluid and rock compositions.

Preliminary calculations reveal that plausible hydrothermal systems on Europa have a high potential for synthesis of organic compounds from inorganic nitrogen and carbon compounds likely to be in Europa's ice (and ocean). As trial approximations to the composition of fresh volcanic material at the base of the Europan ice layer/ocean, these calculations employ host-rock compositions of eucrites, differentiated basaltic meteorites with a source in the asteroid belt. (The presumed eucrite parent body (Vesta) is the closest known basalt-bearing body to Jupiter; it is acknowledged that the parent body is relatively depleted in volatiles (Taylor, 1986), which is certainly not expected for Europa.) Fluid compositions are constrained by models of condensation of volatiles in the protojovian nebula (Prinn and Fegley, 1981). In the results discussed here, the initial water-rich fluid contains 0.3 mole % $CO_2$, 1 mole % $NH_3$, and a trace of HCN.

Reaction-path calculations that simulate heating the Sioux County eucrite in the presence of this fluid from the ice melting point to 300°C yield the equilibrium mineral assemblages epidote + talc + laumontite + quartz + magnetite + paragonite at 100°C, and clinozoisite + fayalite + tremolite + talc + quartz + albite at 300°C. Hydrous minerals compose about 77% of the low temperature assemblage, and about 26% of the high temperature assemblage. A shift in oxidation state with temperature is also revealed by the presence of quartz and magnetite at 100°C and quartz and fayalite at 300°C. In fact, the $f_{O_2}$ of the fluid is more than three log units below fayalite-magnetite-quartz at 300°C. Fluid compositions consistent with these assemblages may allow organic synthesis. For example, metastable equilibrium involving these mineral assemblages and the CHON system (assuming kinetic inhibition of methane and graphite formation) yields abundant acetate, formate, propanoate, butanoate, acetamide, and urea at 100°C, and formate, acetate and methanamine at 300°C.

One implication of these and other model calculations is that hydrothermal systems on Europa are likely to generate altered rocks that have many similarities with altered basalts in the seafloor of the Earth. On the other hand, the fluid compositions (extremely reduced, alkaline pH) are dramatically different from those in black-smoker vents. In addition, the potential for organic synthesis during hydrothermal alteration on Europa is considerable, which may have implications for the composition and physical properties of the lower-most layers of ice, as well as the possibility that living systems could emerge in the dark using chemical energy supplied by the disequilibrium between hydrothermal fluids and molten ice. These calculations also indicate that organic synthesis is a strong function of the oxidation state of the fluids involved, and thus on the assumed compositions of the rock and ice adopted in the model. For example, additional calculations show that mixing of the hydrothermal fluid compositions described above with cooler ocean water (from molten Europan ice) results in the copious production of organic acids at high temperatures, but that greater mixing (and resulting lower temperatures) tends to favour the conversion of the organic acids to bicarbonate, owing to the high oxidation state in $CO_2$-rich ocean.

These calculations illustrate ways in which the alteration products, organic synthesis potential, and life supporting properties of water/rock reactions can be explored for other planets. In general, the following criteria are proposed to test whether a planet is capable of supporting life:

1) Can disequilibrium states derived from water/rock reactions become established? 2) Do these states favour the synthesis of organic compounds from $CO_2$, CO, or nebular condensates? and 3) Are there additional redox disequilibria involving iron and sulphur minerals, and/or iron, sulphur and nitrogen aqueous species that possess sufficient energy to drive metabolic processes?

Answers to these questions will be found by merging methods from geodynamics, igneous petrology, aqueous geochemistry, microbial ecology and bioenergetics. The results will yield predictions of the potential for extraterrestrial life, and pinpoint where to look for it.