Geochemical diversity of hydrothermal systems: Thermodynamic constraints on biology

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Submarine hydrothermal system, once believed to be uniform in composition and temperature, are now realized to be enormously variable in physicochemical conditions (pressure, temperature, as well as composition and electron and proton activities of vent fluids). Because the food webs at hydrothermal vents are primarily supported by energy contained in redox disequilibria, this geochemical diversity will undoubtedly affect biological activity and habitat composition. Chemical differences arise from (1) temporal evolution of systems undergoing supercritical phase separation, (2) differences in basement composition (e.g., basalt, rhyolite, peridotite), and (3) variable influx of magmatic fluids in arc/backarc hosted systems. I will go through the primary differences in vent fluid and hydrothermal precipitate composition and discuss some of the first-order phase relations responsible for the observed geochemical diversity.

In peridotite-hosted systems, high concentrations of dihydrogen and methane and low concentrations of H_2S are directly related to the specific phase equilibria, which lead to the development of low oxygen and sulfur fugacities in the seawater-rock system during serpentinization. Hydrolysis of olivine accounts for the highly alkaline nature of low to moderate temperature serpentinization fluids, while only pyroxenes react at temperature >350°C and set the fluid pH to slightly acidic.

Intra-oceanic arcs and associated backarc basins harbor hydrothermal vents in variable water depth that are extremely diverse in composition because of differences in the temperatures of phase separation and extent of magmatic volatile influx. Just like in on-land hydrothermal springs associated with active volcanoes, three types of fluids are generated within these systems: (1) neutral-pH chloride-dominated fluids, (2) very acidic, sulfate-rich fluids, and (3) moderately acidic, CO_2-rich fluids. Different types of fluids often vent simultaneously from a single volcanic edifice, creating a great geochemical diversity within a small area. Such systems appear particularly well suited for studies of geochemistry-genome relations. A completely different hydrothermal vent type is associated with serpentine mud volcanoes, venting extremely alkaline fluids enriched in hydrogen and hydrocarbons. Like the arc volcanoes, fluid chemistry of the mud volcanoes is ultimately controlled by geological cycling driven by plate tectonics, so that subduction processes directly influence vent chemistry and, hence, biology.

To identify possible chemolithoautotrophic metabolic pathways and biomass production within the spectrum of submarine vents and I used the approach first employed by McCollom and Shock (GCA 61, 4375-4391, 1997) to calculate redox reaction energy yields and potential for biomass production in typical mid-ocean ridge setting (EPR 21°N). While H_2S is the dominant energy source in basalt-hosted mid-ocean ridge vent sites, oxidation of dihydrogen and methane are the reactions with highest energy yields in serpentinization systems. By contrast, ferrous iron and sulfur are important electron donors in the arc/backarc vent fields. The unusal compositions of the arc/backarc vents make them interesting targets in search of unknown metabolisms. For instance, in some of the sulfuric acid springs synproportionation of sulfur is exergonic.

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