Theory on thermodynamic constraints on biogeochemical diversity

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Understanding geographic patterns of biological and geological diversity is central to ecology, evolution, biogeography, and many areas of geology. The number of energy-yielding reactions-geochemical catabolic richnessimposes fundamental constraints on the number of energyyielding reactions harnessed by a living system-the biogeochemical catabolic richness-which in turn can influence organism and ecosystem function and taxonomic diversity. Theory on geochemical and biogeochemical catabolic richness is lacking, despite its relevance to understanding evolutionary and macroecological patterns of functional and metabolic diversity. A system's potential biogeochemical catabolic richness is the number of chemical reactions having energy-yields above some Amin required to make the reaction useful as an energy source. We develop general mathematical theory based in thermodynamics and theoretical geochemistry showing how potential biogeochemical catabolic richness of a reaction system involving a given chemical species depends on temperature, pressure, concentration, Amin, and the frequency distribution of the species' stoichiometric coefficients for the reactions. We then apply the theory to reactions involving H+ to provide mathematical predictions of how the community's potential biogeochemical catabolic richness is a function of temperature, pH, and Amin. We find that the theoretical predictions closely matched empirical richness patterns of hot springs at Yellowstone National Park. The developed theory elucidates the degree to which various physicochemical variables can influence biogeochemical richness, and may have implications for patterns of functional, taxonomic and phylogenetic diversity in microbial communities.

H₂, CH₄ and NH₄ formation through low temperature water-rock reactions in ultramafic rock

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 H_2 , CH_4 and NH_4 are electron donors potentially important for chemolithothrophic microorganisms in subsurface endolithic communities. High-temperature formation of H_2 and CH_4 in ultramafic systems is well studied. Knowledge of low-temperature processes, and the effect of ferrous secondary minerals are however limited. Here we explore the formation of these species during experimental low temperature (25°C) alteration unaltered, medium altered and highly altered dunite from continental sites.

 $\rm H_2$, $\rm CH_4$, $\rm NH_4$ and $\rm NO_3$ were detected in the fluids in all three setups. We suggest that $\rm H_2$ results from reduction of water due to oxidation of Fe(II) released from olivine in unaltered dunite, from brucite and olivine in medium altered dunite, and from brucite and serpentine in highly altered dunite. $\rm CH_4$ may result from abiotic methanogenesis or dissolution of $\rm CH_4$, containing fluid inclusions. The N-species were most likely absorbed to serpentine in the altered dunite, while the source for unaltered dunite is probably explosives used during mining.

The results indicate that water-rock reactions in medium and highly altered ultramafic rocks can provide reduced species potentially supporting microbial communities in lowtemperature subsurface environments in ophiolites and near seafloor parts of ultramafic oceanic lithosphere.