

CONSTRAINTS ON BIOGEOCHEMICAL PROCESSES AND MICROBIAL METABOLISMS FROM HOST ROCK COMPOSITION AND ALTERATION. P.A. Canovas^{1,2} and E.L. Shock^{1,2,3}, ¹GEOPIG, Arizona State University, ²School of Earth and Space Exploration, Arizona State University, ³Department of Chemistry and Biochemistry, Arizona State University.

The alteration of igneous basement rocks produces disequilibria that lead to microbial habitat generation in subseafloor systems. The evolution of fluid compositions and mineral alteration assemblages constrains the availability of energy for microbes and influences the viability of various metabolic pathways. Analyses of the energy supplies available to microorganisms inhabiting these regions can be investigated using existing data on hydrothermal fluids, diffuse fluids, and altered peridotites and basalts. By combining theoretical models of rock alteration with biomolecule synthesis and metabolism, a quantitative approach can be taken toward predicting microbial metabolisms as functions of temperature, pressure, fluid composition, and the extent of rock alteration. These results can be presented in the form of affinity diagrams where conditions of real systems can be plotted to link the nonequilibrium thermodynamics of water-rock alteration with the nonequilibrium processes of metabolism and biosynthesis.

Reaction path modeling shows only slight differences among mid-ocean ridge basalt (MORB) alteration assemblages and the resulting fluid compositions regardless of moderate differences in equilibration temperature, or fairly wide ranges of water-to-rock ratios. As examples, calculated pHs, silica activities and hydrogen concentrations are quite similar even when using MORB compositions that span the range of observations. In contrast, ultramafic assemblages yield far more variability, consistent with experiments and observations of natural systems. To this end, reaction path modeling was performed on host rock assemblages with representative solid solution compositions of olivine, orthopyroxene and clinopyroxene. Results reveal large variations in fluid compositions across olivine-clinopyroxene-orthopyroxene ternary space indicating that dramatic tipping points exist across the compositional variations induced by ultramafic alteration. As an example, model results predict that lowering the temperature from 250° to 2°C for a system with a w:r ratio (kg:mols) of 3:1 decreases the dissolved hydrogen activity by nearly 7 orders of magnitude, but raising it to any higher temperature never results in an increase of more than 2 orders of magnitude above the original value. Conversely, holding the temperature constant and raising the w:r ratio to any value never decreases the hydrogen activity more than 2 orders of magnitude, but lowering the w:r ratio to

1:10 increases the hydrogen activity more than 5 orders of magnitude relative to the initial value.

In a biochemical/synthesis context, the results suggest that energy supply and demand will be modulated by a variety of mineral sources of ferrous iron and the diversity of biochemical reactions microorganisms couple to mineral alteration. For instance, in some systems the syntheses of alkanes, alkenes and some carboxylic and amino acids are thermodynamically favored without the input of energy from microorganisms or their need to couple synthesis to other reactions. However, this is almost never the case for energy-intensive biomolecules such as carbohydrates, purines, and pyrimidines¹. In order to make these compounds, microorganisms need to couple biosynthesis to other reactions. In many hydrothermal systems the energy released by methanogenesis is more than sufficient for the biosynthesis of nicotinamide dinucleotide (NAD), adenosine triphosphate (ATP), and other biomolecules central to metabolism. Other energetic couplings with respect to biomolecules may be explored as well. For example, under conditions associated with low temperature alteration environments, thermodynamic calculations indicate that there is sufficient drive to support the reduction of NAD via hydrolytic oxidation of ferrous minerals. Reactions using ferrosilite to meet energetic demands are more or less favorable than those using fayalite depending on the conditions where they occur. Overall, microbes will meet their energetic demands through various coupled biogeochemical pathways, depending on the details of the system they inhabit. As a consequence, coupled metabolic processes will shape the reaction paths, rates, and extents of microbial alteration that various systems undergo, as well as overall biological productivity and diversity. Modeling results such as these can indicate how a system can engender habitable environments where abiotic synthesis, metabolic processes, or even the emergence of life is or is not possible.

References: [1] Shock E.L. and Canovas P.C. (2010) *Geofluids*, 10, 161-192.