

Microbial weathering of ocean crust

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The oxidative weathering the rock type that represents the largest fraction of Earth's crust, oceanic basalt, involves a large change in free energy. If harnessed by microbes, significant biomass production may be supported. However, basalt rock habitats, remain poorly studied with respect to the microbial communities that may be supported by oxidative weathering. We are examining the early stages of ocean crust alteration using molecular microbiological, theoretical energetic, and mineralogical approaches.

Energetic calculations suggest that most biological activity in the ocean crust should occur in close proximity to spreading centers on ridge flanks where low-temperature fluid circulation is substantial. In these environments, abundant reduced basalt is in contact with oxidized fluids. Combined, aerobic and anaerobic reactions involving Fe, S, and H₂ may result in biomass production of up to one million tons of C per yr rocks aged less than 10 M.a. (Bach and Edwards, 2003). Biological activity likely declines significantly off-axis in older, highly altered crust (>10 Ma) due to the depletion of either suitable oxidants or reductants.

16S rRNA and electron microscopy studies have been conducted on the bacterial fraction of the microbial communities colonizing very young (<1 M.a.) basalt samples that displayed varying degrees of weathering. Diverse, yet distinct populations of bacteria were detected on the different samples. A general trend moving from more metal and S-oxidizing autotrophic communities towards more metal- and S-reducing populations as the samples accumulated more weathering products is suggested. Our studies indicate that a succession of microbial populations on basalt occurs during weathering and that metal, S, and C cycling are prominent characteristics of basalt-hosted cryptoendolithic microbial communities at the seafloor.

Oxidant production via electron bombardment: Progress in experimental simulations of the European surface environment

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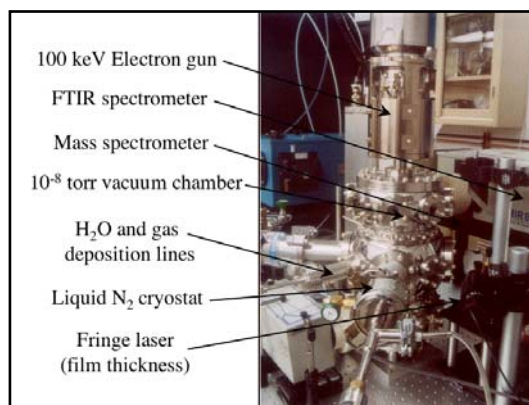
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At present our understanding of the European system indicates that both liquid water and a suite of biogenic elements should be available in the European hydrosphere. Considering the habitability of the putative ocean, the major limiting resource may very well be available free energy [1].

As a result of being situated deep within the Jovian magnetosphere, the surface of Europa is exposed to high energy, charged particle irradiation. The incident particle flux of 7.9×10^{10} keV cm⁻² s⁻¹ is dominated (>75%) by electrons in the keV to MeV range [2]. Ground based measurements and data from the Galileo Near-Infrared Mapping Spectrometer (NIMS) have revealed a suite of radiolytically produced oxidants at the surface (including O₂, CO₂, SO₂, H₂O₂) [3-5].

In order to replicate some of the chemical processes occurring on the surface of Europa, we have constructed a vacuum chamber equipped with a high-energy electron gun and a cryostat vapor-deposition plate (see figure). Electron irradiation of water ices has produced hydrogen peroxide and preliminary results indicate percent abundances of H₂O₂ greater than those estimated from surface observations of Europa. Implications for a subsurface ecosystem will be discussed.



References

- [1] Chyba, C. F. (2000) *Nature* **403**, 381-382.
- [2] Cooper, J. F., et al. (2001). *Icarus* **149**, 133-159.
- [3] Spencer, J. R. et al. (2002) *Astron. J.* **124**, 3400-3403.
- [4] Carlson, R. W., et al. (1999) *Science* **286**, 97-99.
- [5] Carlson, R. W. et al. (1999) *Science* **283**, 2062-2064.

Anaerobic oxidation of natural gas in soil – The geochemical evidence?

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Natural gas (>99 vol.% CH₄) leaks along the well bores of ca. ½ of the oil wells in W. Canada. Leaking gas reaches the unsaturated zone where it is partially to completely consumed by aerobic bacteria. Long term monitoring of soil gas contents near two wells drilled in 1997 demonstrates that aerobic oxidation produces up to 20 vol. % CO₂ and reduces CH₄ levels near the soil surface to 0.01 vol. %. The O₂ content below 100 cm falls to 0.1 vol. %.

Small amounts of authigenic calcite (0.02 to 8.0 g/kg) of bacteriogenic and abiotic origin have formed in the soil near the wells. Low δ¹³C_{calcite} (-30 to -57 ‰, PDB) indicates that CH₄ is the predominant carbon source. Low δ¹⁸O_{calcite} (-17 to -22 ‰, PDB) suggests isotopic disequilibrium consistent with estimated rapid growth rates and with the involvement of bacteria with calcite precipitation. The discovery of pyrite framboids and authigenic calcite in soil close to the well bore indicates that the two minerals formed in an anaerobic environment likely as a result of anaerobic oxidation of methane (AOM). The latter is corroborated by the higher authigenic calcite content and higher than background pH (by 0.5-2.9 units) of soil samples close to well bores. Elevated pH is likely related to HCO₃⁻ production during AOM. In contrast, soil samples collected further away from the well bores contain little or no authigenic calcite and have lower than background pH likely related to the high soil CO₂ concentrations produced during the aerobic oxidation of CH₄.

The small amounts of authigenic calcite suggest that AOM may be confined to rare isolated domains in the soil where anaerobic conditions are maintained by flushing of natural gas and by O₂ consumption associated with aerobic oxidation of CH₄. In vitro assays with soil samples collected near the wells have not shown CH₄ based sulphide production so far. The limited sulphur availability in the soils and the low free energy yield of SO₄²⁻ reduction driven OM render other species (e.g.; Fe³⁺) more likely to be used as preferred electron acceptors. Important advantages of Fe³⁺ are its greater availability in soil and that it may readily be re-supplied through regeneration especially if Fe²⁺ resides in soil as carbonate or green rust.

What's on the menu for thermophilic heterotrophs?

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Chemotrophy is the energetic foundation of microbial communities in most hydrothermal systems. However, the diversity of energy sources in these hydrothermal systems is only poorly understood because the requisite analyses of thermal fluids and minerals are rare. In particular, there is a paucity of measurements of organic compounds that are needed to determine the energetics of heterotrophic metabolisms.

Concentrations of aqueous amino acids (0-28 μM) [1], sugars (0-23 μM), and organic acids (0-32 μM) [2] were recently determined in vent fluids at Vulcano Island, Italy. Together with earlier analyses of inorganic solutes, gases and minerals, and standard state properties, *in situ* values of ΔG, were calculated for 115 organic oxidation reactions at 6-8 sites at Vulcano. The terminal electron acceptors considered in these computations were O₂, SO₄²⁻, S⁰, NO₃⁻, and Fe(III) in magnetite. All reactions considered were exergonic (energy-yielding) at all of the sites investigated, with the highest energy yield from the aerobic oxidation of the amino acid arginine (-162 kJ/mol e⁻ transferred). In general, oxidation with O₂ yielded the most energy (98-162 kJ/mol e⁻), followed by NO₃⁻ (61-118 kJ/mol e⁻) and Fe₃O₄ (26-125 kJ/mol e⁻). Oxidation with SO₄²⁻ or S⁰ yielded only (6-46 or 11-59 kJ/mol e⁻, respectively), despite the ubiquity of sulfur metabolisms in thermophilic communities. Reactions with each terminal electron acceptor yielded similar energies (normalized per electron transferred) for the oxidation of amino acids, sugars and organic acids, as well as for the oxidation of CH₄ and CO. Differences in reaction energetics across the sites depended primarily on variations in geochemical compositions and not temperature.

References

- [1] Svensson, E., Skoog A. and Amend J. P., (2004). *Org. Geochem.* **35**, 1001-1014.
- [2] Amend J. P., Rogers K. L., Meyer-Dombard D. R., (2004). *GSA Special Paper* **379**, 17-34.

Thermodynamic analysis of microbial metabolism in hydrothermal systems

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By catalyzing a wide variety of oxidation-reduction reactions, subsurface communities of microorganisms have a significant impact on their geologic environments. To better understand this impact, we have developed a quantitative thermodynamic model describing microbial coupling of irreversible redox reactions to otherwise endergonic biochemical reactions responsible for synthesizing biomass at elevated temperatures and pressures. Because microbes consist of approximately 80% protein and nucleic acids by dry weight, we have focused on quantifying the conversion of environmentally available energy into these biomacromolecules from their constituent monomers, amino acids and nucleotides, respectively.

The flow of electrons in a microbe resulting from any type of catabolic strategy is, through a complicated set of reactions, coupled to the synthesis of ATP, the universal energy currency of all cells. Organisms in turn couple the Gibbs free energy-liberating hydrolysis of ATP and other nucleotide triphosphates to the energy-demanding dehydration reactions required to polymerize proteins and nucleic acids. Hence, quantitative description of the synthesis of ATP by way of electron flow and the biosynthetic demand-driven hydrolysis of ATP is crucial to understanding the energetics of microbial growth. The microbial coupling model developed in the present study can be used to quantify the polymerization of proteins and nucleic acids in terms of the flow of electrons from any donor to any acceptor and the subsequent synthesis of ATP from ADP. We present the results of calculations that can be used to determine the production of microbial biomass generated in terms of nucleic acids and proteins in a variety of environments characterized by differing temperatures, pressures, and bulk compositions.

Energetic constraints on subsurface biomass production within the igneous ocean crust

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Deep-sea hydrothermal vents have long been recognized to host prolific biologic communities that rely on chemical energy as their source of primary biomass production. More recently, it is becoming increasingly apparent that the high-temperature vents may just be the tip of the biological iceberg, and that there may be substantial biomass living below the subsurface along mid-ocean ridges and within the basaltic crust. Owing to the scarcity of organic material in seawater and basaltic rocks, any substantial biologic communities living within the subsurface must also rely primarily on chemical sources of energy.

Subseafloor environments are just in the early days of exploration. Consequently, little is yet known about what organisms live there, how many there are, where they live, or what their metabolic activities are. However, because these communities are likely to be largely dependent on chemical sources of energy, we can gain some insight into the likely abundance, spatial distribution, and metabolic activities of subsurface microbial populations by examining the sources of chemical energy that are available to support the community.

I will present results of an energetic evaluation of several different seafloor habitats that owe their existence to ongoing hydrothermal and geologic processes along mid-ocean ridges, including diffuse subsurface mixing zones, weathering of rocks on the seafloor, downflow zones, and low-temperature alteration of basalt. Diffuse mixing zones, where high-temperature hydrothermal fluids mix with seawater in the subsurface on the flanks of hydrothermal vents, are likely to be the most productive subsurface habitats, with sufficient energy to support biological production much larger than occurs at the well-studied hydrothermal chimneys. Oxidation of rocks at the seafloor and in downflow zones also has the potential to support substantial populations of microbes. In contrast, there is relatively little energy available to hydrogen-based methanogenic communities like those that have been proposed to exist in terrestrial basalt aquifers, suggesting this type of environment makes relatively little contribution to total subsurface microbial carbon fixation. Altogether, there is sufficient energy in seafloor environments to support about 10^{12} g (dry wt) of primary biomass production per year.

Organic sulfur compounds in extremophile metabolisms

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Sulfur is a key component of metabolic and biochemical processes in many organisms that inhabit extreme environments. Inorganic sulfur redox reactions are nearly ubiquitous in the metabolisms of known thermophiles and use of reduced organic sulfur compounds may also be common. In low temperature environments, both methanogens and sulfate-reducers have been shown to metabolize dimethylsulfide (DMS) and methanethiol (MSH) (Tanimoto & Bak, 1994). Given that methanogens and sulfate reducers are also found in high temperature environments, it is likely that DMS, MSH and other reduced organic sulfur compounds are energy sources in hydrothermal systems. However, the energy yields of metabolic reactions among organic sulfur compounds under hydrothermal conditions have not been investigated.

Building on our earlier work on thiols (Schulte & Rogers, 2004), we have compiled and estimated thermodynamic properties for alkyl sulfides. We are investigating reactions among various sulfur compounds in a variety of extreme environments, ranging from sea floor hydrothermal systems to organic-rich sludge. Using thermodynamic data and the revised HKF equations of state, along with geochemical constraints imposed by extreme environments, we are able to estimate the abiotic production of organic sulfur compounds. In hydrothermal systems in which H₂ and H₂S concentrations are buffered by the PPM mineral assemblage, equilibrium activities of DMS are as high as 10⁻³ through formation with millimolar concentrations of CO₂. Higher activities are obtained when DMS formation from CO is considered. We also calculate the amount of energy that would be available to putative DMS- and MSH-metabolizing organisms in hydrothermal environments.

References

- Kiene R.P., Oremland R.S., Catena A., Miller L.G. & Capone D.G. (1989) *Appl. Env. Microbio.* **52**, 1037-1045.
Schulte M.D. & Rogers K.L. (2004) *GCA* **68**, 1087-1097.
Tanimoto Y. & Bak F. (1994) *Appl. Env. Microbio.* **60**, 2450-2455.