Geochemistry at the biotic fringe

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As the subsurface biosphere is explored, we realize that life on the Earth is accompanied by life *in* the Earth. Sensing the subsurface biotic fringe relies on detecting major geochemical consequences that accompany the biological transitions where the sterile interior of the Earth becomes populated. Deep life gains energy for growth and reproduction from chemical sources, which exist because geologic processes bring together constituents that are far from oxidation-reduction equilibrium with one another. The hard limits to life in this dark biosphere are not known, but can not exceed conditions where the rates of oxidation-reduction reactions occur so quickly without catalysis that biology stands nothing to gain. We can guess that these limits will differ depending on the nature of the oxidation-reduction reaction involved, including numbers and mechanisms of electron transfer and details of bond breaking and reorganization that permit energy to be tapped. Attainment of equilibrium can be sluggish for reactions involving transfer of large numbers of electrons. As an example, the time required for methane and carbon dioxide to be brought to equilibrium in the laboratory is only practical at temperatures > 400°C, and several lines of compositional and isotopic evidence point to methane-CO_2 disequilibria below similar temperatures in hydrothermal systems. The mechanistic complications of this eight electron transfer allow autotrophic methanogens to catalyze the coupled reduction of carbonic acid to methane with the oxidation of hydrogen to water. Away from the temperatures of oxidation-reduction equilibrium, disequilibria generally increase until microbial processes begin to dissipate the available energy. Extrapolating from measured temperatures of inhabited hydrothermal ecosystems to apparent temperatures of equilibration for oxidation-reduction reactions allows identification of links between microbial dissipation of energy sources and geochemical signatures of the deep biosphere.

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Does oxic metabolism control substrate availability for terrestrial methanogenesis?

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We use the carbon isotopic composition of pore water dissolved inorganic carbon (DIC) to calculate rates of methane production and oxidation in Sallie's Fen, a New Hampshire wetland. We employ a simple model of reaction and transport to reproduce the isotopic profiles in addition to the measured DIC and CH_4 concentration profiles. This method allows us to calculate the rates of methanogenesis as a function of depth occurring *in situ* within the peat profile. We find that these isotope-constrained rates of methane production cannot explain the high summer methane emissions measured from static flux chamber data from this site (Varner and Crill, unpublished data), underestimating methane fluxes by approximately 10 to 50 times. Neither horizontal advection, nor uncertainties surrounding the fractionation factors, can explain this discrepancy. We hypothesize that the missing methane is produced and released from the top 1 to 5 cm, and that episodic mixing, and subsequent gas exchange at these depths, prevents both the concentration and carbon isotopic signals of this methanogenesis from penetrating deeper into the profile. Substrate limitation is a common theme in methanogenesis literature but is rarely discussed as an ecosystem-scale control. *In situ* experiments at Sallie's Fen showed stimulation of methane production at depth due to acetate injections while no response was found from similar injections of phosphorous or ammonia. Our findings suggest that the rate of oxidative degradation of organic matter may be controlling the rates of substrate flow to methanogenesis and limiting methane production in this setting. As the oxic boundary penetrates deeper into the pore water profile during the colder months, our data captures this interface, and we find maximum rates of methane production occurring just below the zone of methane consumption. We suggest that methanogenesis is limited by the availability of substrate material, the production of which depends on oxygen availability. If this is correct, it suggests a very fast timescale for terrestrial methane source response following abrupt climate change, such as those observed in the Greenland ice cores.