

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.