

Testing the “deep-basin high-rank gas machine” hypothesis

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During the past decade the interest in a more detailed understanding of processes during gas and oil formation has been spurred by growing importance of gas and oil from unconventional reservoirs, e.g. shale gas and shale oil as well as deep basin-centered gas. In addition to the classical view of mainly first-order reactions for the inorganic formation of hydrocarbon gases by thermal cracking of bitumen or kerogen, several researchers have put forward avenues to explain some not accounted for observations in hydrocarbon occurrences, molecular or isotopic compositions. These hypotheses always include a geologic component not considered in most kerogen/bitumen pyrolysis studies: The presence and role of water [1], the possible catalytic activity of mineral surfaces [2], the importance of metals in aqueous fluids, the metastable equilibria of hydrocarbons and more oxidized organic compounds in pore-fluids in the subsurface – and the role of minerals as part of pore-fluid redox- or pH-buffers [3]. Price [4] combined many of the aforementioned hypotheses in calling for a “deep-basin high-rank gas machine”.

A broad study to produce a consistent data set of HC formation rates and elemental transfer reactions in the gas-fluid-rock system at elevated pressures and temperatures is ongoing at the BGR. By using different experimental facilities for maturation of organic matter from small gold capsules to Dickson-type flexible gold-titanium cells in high-pressure reactors to large diameter high pressure reactors for heating/expulsion tests on core material several key questions are being addressed.

The experiments with source rock material of natural maturity series allowed the detailed comparison of effects of natural medium-temperature/high-pressure maturation in the sedimentary basin to artificial high-temperature/high-pressure maturation in the lab. Interestingly, a clear depiction of the predominance of different processes – e.g. thermal cracking, oxidation reactions to less reduced organic compounds, dehydrogenation by cyclization and aromatization - is visible in the data sets. The comparison of sets of experiments with the identical amounts of source rock material with/without the admixture of different mineral standards – e.g. carbonate, pyrite, montmorillonite – yielded clues about the role of certain mineral surfaces for catalytic oxidation/dehydrogenation/hydrogenation and fluid buffering. Using organic model compounds with isotope labels added to the source rocks clearly identified pathways of hydrocarbon gas formation – and the production of more oxidized organic compounds.

[1] Lewan (1997) *Geochim. Cosmochim. Acta* **61**, 3691-3723. [2] Mango *et al.* (1994) *Nature* **368**, 536-538. [3] Seewald (1994) *Nature* **370**, 285-287. [4] Price (1997) USGS DS **67**, H.

Anaerobic methane oxidation in the water column of the eutrophic sub-alpine Lake Zug (Switzerland)

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Anaerobic oxidation of methane (AOM) remains only partially understood in freshwater environments. Water column field investigations suggest that AOM could be mediated via other pathways, i.e. denitrification or metal oxide reduction, in lakes [1, 2], as opposed to its marine counterpart, where AOM proceeds via SO_4^{2-} reduction [3].

The potential for AOM was assessed in the water column of the eutrophic sub-alpine Lake Zug, situated in Central Switzerland. Through geochemical profiling and flux calculations of the relevant factors, the oxic/anoxic transition zone and anoxic depths, showing favorable conditions for AOM, were identified. At these selected depths, incubation experiments were carried out with ^{13}C -labelled methane to determine methane oxidation rates, simultaneously in-situ available electron acceptors were monitored. Fluorescence in-situ hybridization targeting Group I and II as well as anaerobic methanotrophs was carried out at the incubation depths. Furthermore, functional gene analysis for particulate (*pmoA*) and soluble methane monooxygenase (*mmoX*), both essential for aerobic methanotrophs, and methyl coenzyme M reductase (*mcrA*), an indicator for anaerobic methanotrophs, was completed.

Preliminary experiments show that AOM rates are one order of magnitude higher ($\sim 600 \text{ nM}\cdot\text{d}^{-1}$) than aerobic rates ($\sim 40 \text{ nM}\cdot\text{d}^{-1}$). Highest rates occur at depths, which are devoid of oxygen. First results are still inconclusive as to which electron acceptor is responsible for AOM, however, SO_4^{2-} does not appear to contribute substantially. Hybridization techniques confirm the presence of Type II alpha-proteobacterial methanotrophs as well as Group I and II methanotrophs.

[1] Schubert *et al.* (2010) *Aquatic Sciences* **72**, 455-466. [2] Crowe *et al.* (2011) *Geobiology* **9**, 61-78. [3] Boetius *et al.* (2000) *Nature* **407**, 623-626.