4.4.24

## Sulfate reduction and anaerobic oxidation of methane in hydrothermal sediments of Guaymas Basin

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Hydrothermal sediments of the Guaymas Basin contain a high diversity of anaerobic thermophilic microorganisms, including methanogens, sulfate reducing bacteria and presumably also methanotrophs. Thermogenic reactions in the subsurface sediments provide a complex mixture of methane, higher hydrocarbons and volatile fatty acids which can be utilized by these microorganisms.

While sulfate reduction (SR) was already identified to be an important process in Guaymas Basin sediments, anaerobic oxidation of methane (AOM) was only identified indirectly through genomic analysis and occurrence of certain biomarkers. This study is the first direct evidence that AOM occurs at elevated temperatures.

By using refined techniques both processes were measured with radioactive methane and sulfate as trace substrates at temperatures of  $5-200^{\circ}$ C and pressures of 1, 220 and 450bar. Maximum sulfate reduction rates (SRR) of almost 6700 nmol cm<sup>-3</sup> were measured at 60-90° C and 450 bar. Maximum rates of AOM were observed at 35-90 °C but generally accounted for less than 5% of SR. Apparently carbon sources other than methane are preferred although its presence in high concentrations.

## 4.4.31

## The deep biosphere's imprint on carbonate carbon isotope systematics in basalts from the seafloor

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Basalts of the oceanic crust commonly contain thin calcite veins and vesicles in the pillows may be filled by carbonates. Numerous isotopic studies have shown such secondary carbonates to have  $\delta^{13}$ C near 0% and temperatures calculated from their  $\delta^{18}$ O suggest deposition from very low-temperature seawater permeating through the oceanic crust. However, a very different isotope pattern is found for disseminated carbonates from the glassy margins of the pillows. There the carbonates are much less abundant, have negative  $\delta^{13}$ C, and temperatures calculated from $\delta^{18}$ O suggest formation at much warmer to hot temperatures. Petrographic observations, X-ray element mapping, and DNA staining indicate that these glassy margins are being bioaltered. We suggest the generally low  $\delta^{13}$ C (< -7%) of disseminated carbonates in basaltic glass are metabolic byproducts of Bacteria, formed by oxidation of dissolved organic matter in pore waters with an optimal growth temperature near 70°C. A few positive  $\delta^{13}$ C have been observed. These come from slow-spreading ridges and suggest in those settings lithotrophic utilization of CO2 in which methanogenic Archaea produced CH<sub>4</sub> from H<sub>2</sub> and CO<sub>2</sub>.

The  $\delta^{13}$ C contrast between pillow margins and interiors is a robust biomarker for ancient sub-seafloor life in metamorphosed and dismembered ophiolites. The more obvious petrographic and genomic indicators of bio-activity are commonly lost through devitrification of glass but the carbonate $\delta^{13}$ C contrasts may be preserved. Microbial glass alteration is evident both optically and isotopically in relict glass from Cretaceous to Ordovician ophiolites altered under greenschist facies and lower metamorphic conditions but nucleic acid staining failed. Greenschist facies pillow rims from a Caladonide ophiolite have retained isotopic as well as some textural evidence of bioalteration of glass. The described  $\delta^{13}$ C biosignatures are even found in the formerly glassy margins of Proterozoic and Archean ophiolites pillow lavas where few if any textural indicators remain. (Eclogite facies metamorphism has however, homogenized  $\delta^{13}C$  of pillows from Corsica.) We suggest that cross-pillow  $\delta^{13}$ C contrasts may serve as a biomarker in the Earth's earliest submarine basalts, which according to some theories may have been the cradle of life itself.