

## Biogenic methane and bacterial community structure in Ordovician shales, Michigan Basin, Ontario

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As a component of geoscientific investigations for a deep geological repository in Middle Ordovician strata of the Michigan Basin near Tiverton, Ontario, methane from hypersaline pore waters ( $Cl^- > 6$  molal) in shale and limestone core samples was analysed for concentration,  $\delta^{13}C$  and  $\delta D$ .

$CH_4$  is highly depleted in  $^{13}C$  and  $D$  from the top of the Queenston Formation down through the Cobourg Formation. Based on the location of the isotopes on a discrimination diagram for methane, the isotopes are interpreted to be of biogenic origin. An associated zone of  $^{13}C$ -enriched  $CO_2$  strengthens this interpretation and constrains production to the lower Georgian Bay and upper Blue Mountain formations. The  $\delta^{13}C$  and  $\delta D$  signatures of methane from the limestones below the Cobourg Formation increase sharply to values consistent with methane of thermocatalytic origin.

In an attempt to resolve whether methanogenic archaea may still be active in these strata, environmental DNA was extracted from core samples and PCR amplified using 16S rDNA primers. PCR performed with archaeal 16S rDNA and methanogen-specific (*mcrA*) primers yielded no DNA, whereas low, but measurable, yields were obtained for bacterial primers. Gene analysis indicated that bacterial sequences similar to *Proteobacteria*, *Cyanobacteria*, *Firmicutes*, and *Actinobacteria* were present.

The majority of identified bacterial species were uncultured extremophilic heterotrophs. We believe that identified bacteria have survived in the rocks for a prolonged period of time by utilizing available energy sources that were trapped during deposition or by assuming a state of dormancy. In contrast, methanogenic archaea are considered to be halophobic and their absence today is not surprising. We hypothesize that the biogenic methane in the Upper Ordovician shales is of para-diagenetic origin, and has been preserved in-situ for some 400 My.

## Sulphur isotopy in a sequence of iron-limited organic rich deposits

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In the Negev, the transition from latest Campanian to early Maastrichtian is marked by organic- and phosphate-rich sediments deposited in a high productivity regime induced by coastal up-welling along the southern margin of the Tethys. The study aims at tracing small scale fluctuations in the depositional conditions in this coastal upwelling system, by exploring the isotopic composition of different forms of sulphur in a ca. 50 m thick sequence, encompassing the top of the Phosphate Unit (PU) of the Mishash Formation and the Oil Shale Member (OSM) of the Ghareb Formation.

Different sulphur compounds, including acid soluble sulphates (ASS), acid volatile sulphides (AVS), chromium reducible sulphur (CRS), organic sulphate (OS) and organic bond reduced sulphur (ORS) were separated according to the protocol suggested by Mayer and Krouse [1] and were characterized for their isotopic composition.

In oil shales most of the sulphur (up to 94%) is bound to the organic fraction, decreasing gradually toward the top of the OSM to 40-60% of the sulphur present in sediment. Pyrite-S (CRS), which is the second most common form of sulphur, is low in the basal, most organic rich part of the OSM (<10%), but it can represent up to 40-50% of sulphur in the central part of the section. In the PU and in the marls that top the oil shales, sulphate-S (gypsum, apatite-bound-S) becomes the dominant S-species (>80% of total).

The  $\delta^{34}S$  values of the reduced organic sulphur vary throughout the section in a relatively close range between -6 and +1‰, and are always considerably higher than the much more scattered values recorded for the pyrite-S. Sulphur in pyrite is typically strongly depleted in  $^{34}S$  (-43 to -34‰), except in the PU and in the lowest, most organic-rich part of the OSM where the  $\delta^{34}S$ -values can be as high as -16‰.

The incorporation of sulphur into sedimentary pools with distinct isotopic composition is interpreted in terms of depositional conditions/ primary environmental signals (e.g., availability of reactive iron and degradable organic matter, sulphate diffusion, bottom water oxygenation, sedimentation rate) which were in part overprinted by late/ post diagenetic effects.

[1] Mayer, B. & Krouse, H.R. (2004) In: Procedures for Sulfur Isotope Abundance Studies (ed. P.A. de Groot.) *Handbook of stable isotope analytical techniques*. pp. 538-596.