

## Tracking microbial life in the marine subsurface

TOBIAS GOLDHAMMER AND MATTHIAS ZABEL

Research Center Ocean Margins, FB5 Geosciences, University of Bremen, PBox 330440, 28334 Bremen, Germany (goldhammer@uni-bremen.de, mzabel@uni-bremen.de)

Evidence has grown that deeply buried marine sediments are habitats to living communities of microorganisms, even under scarcity of nutrients and terminal electron acceptors and apparently hostile environmental conditions. The contribution of such communities to element cycling remains elusive, but direct microbiological assays are difficult to conduct due to extreme in situ conditions. We suggest to make use of anorganic, cell-independent proxies to bypass this hassle and propose the application of oxygen stable isotopes of dissolved inorganic phosphate (DIP) in marine pore waters.

The  $^{18}\text{O}/^{16}\text{O}$  ratio of pore water DIP is significantly affected by active microbial phosphate ( $\text{PO}_4$ ) metabolism. The exchange of oxygen atoms between water and phosphate is enhanced by extra- and intrazellular hydrolase enzymes in living cell  $\text{PO}_4$  uptake and processing, and can be distinguished from abiotic fractionations during sediment diagenesis (Blake *et al.* 2005). Therefore we consider the  $\delta^{18}\text{O}$  of pore water DIP a fairly robust and feasible parameter for the identification and profiling of microbial activity in deep sediment cores.

We here present a modified microextraction technique for marine pore water  $\text{PO}_4$ . DIP is concentrated by magnesium induced coprecipitation, separated from interfering anions by a preparative ion chromatography using anion exchange resin, and subsequently precipitated as silver phosphate ( $\text{Ag}_3\text{PO}_4$ , Colman 2002).  $\text{Ag}_3\text{PO}_4$  is finally combusted in an elemental analyzer, and transferred online via continuous flow to an isotope ratio mass spectrometer. The amount of DIP required for the precipitation of crystal  $\text{Ag}_3\text{PO}_4$  can thereby be reduced to less than 1mg, making an analysis of pore water samples which are limited in sample volume and DIP content possible. On research cruise MSM04-4a with German vessel Maria S. Merian we recovered four sediment cores up to 42m below sea floor offshore Morocco using a remotely operated seafloor drill rig, and took pore water samples with an average depth resolution of 0.5m for the application of the novel technique described above.

### References

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Colman A.S., (2002), PhD thesis, Yale Univ.

## Experimental $\text{CO}_2$ and water interactions with Permian coals of Queensland, Australia

S.D. GOLDING<sup>1</sup>, P. MASSAROTTO<sup>2</sup>, R. IYER<sup>2</sup>,  
K.A. BAUBLYS<sup>1</sup> AND V. RUDOLPH<sup>2</sup>

<sup>1</sup>Earth Sciences, University of Queensland, QLD 4072, Australia (s.golding@earth.uq.edu.au)

<sup>2</sup>Chemical Engineering, University of Queensland, QLD 4072, Australia (paulm@cheque.uq.edu.au)

A key issue for geological sequestration of  $\text{CO}_2$  is the effect of geochemical reactions between multi-phase fluids and the host strata. We report here the results of batch experiments conducted under simulated in situ conditions (38°C and 90 bar for 60 hrs) to evaluate the chemical and physical changes caused by  $\text{CO}_2$  injection into deep coal seams. Experiments were conducted in a purpose built reactor on coal blocks (15 mm to a side) and powders (180-220  $\mu\text{m}$ ) using supercritical  $\text{CO}_2$  and water ( $\text{SCO}_2\text{-H}_2\text{O}$ ), supercritical  $\text{CO}_2$  ( $\text{SCO}_2$ ) and water ( $\text{H}_2\text{O}$ ) alone. The Permian coals used in this study were of similar rank but quite different texture. Coal A has a vitrinite reflectance of 0.9% and is a dull, relatively massive coal. Coal B has a vitrinite reflectance of 0.85% and is a bright, well banded coal.

Leachate chemistry indicates significant mobilisation of metals that results from dissolution of sulfide, carbonate and silicate minerals and displacement of cation exchangeable metals from coal.  $\text{CO}_2$  alone and  $\text{H}_2\text{O}$  alone mobilise less mineral matter than  $\text{SCO}_2\text{-H}_2\text{O}$  and have less impact on coal density and porosity. SEM images provide evidence of dissolution of cleat and matrix minerals that continues during a second 60 hour treatment with  $\text{SCO}_2\text{-H}_2\text{O}$ . The 15mm cubes behave differently to each other when treated with  $\text{SCO}_2\text{-H}_2\text{O}$ . The bright coal cubes show a decrease in helium density, whereas the dull coal cubes show an increase in helium density. This indicates that coal character influences swelling behaviour and the extent of mineral matter mobilisation. The decrease in helium density and increase in surface areas for the bright coal cubes and coal powders suggests that dissolution of mineral matter in the near injection well area may counterbalance reduction in permeability due to swelling as a result of adsorption of  $\text{CO}_2$ .