Phosphate oxygen isotopes and microbial activity in the marine subsurface

T. GOLDHAMMER[1]*, B. BRUNNER[2], T. FERDELMAN[1,2] AND M. ZABEL[1]

[1]MARUM Center for Marine Environmental Science, University of Bremen, 28359 Bremen, Germany (*correspondence: goldhammer@uni-bremen.de) (mzabel@uni-bremen.de)
[2] Max Planck Institute for Marine Microbiology, 28359 Bremen, Germany (bbrunner@mpi-bremen.de, tferdelm@mpi-bremen.de)

The oxygen isotopic composition of dissolved phosphate (PO_4) in marine pore waters is altered during microbial PO_4 cycling by a number of factors. Equilibrium isotopic exchange between PO_4 and water (H_2O) is catalyzed by enzymes that hydrolyze PO_4 from organic matter, and manage cell-internal turnover of phosphorylated biomolecules (ATP/ADP, APS, polyphosphates). Such equilibria depend largely on the prevailing enzymatic systems [1] and are controlled by ambient temperature [2]. Kinetic fractionation during PO_4 uptake may play an additional albeit minor role. It has thus been proposed to employ PO_4-$\delta^{18}O$ as an inorganic biomarker [3].

So far, obtaining data of pore water PO_4-$\delta^{18}O$ has been difficult because sample PO_4 quantities were too small for conventional sample preparation. We use a multi-step extraction that allows the transformation of < 1 µmol of interstitial water PO_4 to Ag_3PO_4 for subsequent isotope analysis. We profiled PO_4-$\delta^{18}O$ in two sediment cores of the Northwest African margin (< 40 mbsf) and obtained to our knowledge the first dataset on pore water PO_4-$\delta^{18}O$. Important features of the profiles are an occurence of isotopically lighter PO_4 than expected from equilibria considerations in the upper layers of the sediments and a slight downcore trend towards heavier PO_4 with values generally in a range previously described for isotopic equilibria in microbial PO_4 turnover.

We hypothesize that the isotopic disequilibria indicate incomplete PO_4 cycling expressed by a combination of effects: (1) a non-steady state exchange of the oxygen between PO_4 and H_2O, *e.g.* when high mineralization and PO_4 release rates exceed microbial PO_4 uptake, (2) inheritance/dilution effects of isotopically different source of PO_4, and (3) previously unknown enzymatic effects.

[1] Blake *et al*. (2001) *PNAS* **98**, 2148-2153. [2] Longinelli *et al.* (1976) *EPSL* **32**, 389-392. [3] Blake *et al*. (2005) *AJS* **305**, 596-620.

Natural analogues for storage of CO_2 in coal systems, Gunnedah and Bowen Basins, Australia

S.D. GOLDING[1]*, I.T. UYSAL[1], Y-X. FENG[2], K.A. BAUBLYS[1] AND J.S. ESTERLE[1]

[1]Earth Sciences & CO2CRC, University of Queensland, QLD 4072, Australia (*correspondence: s.golding1@uq.edu.au)
[2]Centre for Microscopy and Microanalysis, The University of Queensland, QLD 4072, Australia

Coal bed methane (CBM) fields in sedimentary basins are possible storage sites for anthropogenic CO_2 with the added economic benefit of enhanced recovery of CBM. CO_2 can also be stored in deep unmineable coal seams although this option is less attractive because of injectivity issues and the lack of an economic byproduct. Natural accumulations of CO_2 in coal seams are commonly derived from inorganic sources and provide natural analogues for predicting the long term behaviour of CO_2 in coal geosequestration systems.

We have dated illitic clay minerals associated with calcite-ankerite mineralisation in the Gunnedah and Bowen Basins using the Rb-Sr method. Illite fractions from a high CO_2 hole in the Oaky Creek area have a Rb-Sr isochron age of 208±5 Ma. These Rb-Sr data together with comprehensive K-Ar and Rb-Sr geochronology from across the Bowen Basin indicate clay-carbonate precipitation from CO_2-rich meteoric fluids during the Late Triassic regional extension. On the other hand, Rb-Sr data for Gunnedah Basin illites have ages of 85±4 Ma and 94±1 Ma that reflect heat and CO_2 release from local magmatic intrusions in the Late Cretaceous.

Sr isotope and rare earth element (REE) data for the Gunnedah Basin samples indicate that the majority of calcite-ankerite and dawsonite precipitated from fluids that had interacted with or been derived from relatively young igneous intrusions. Much higher $^{87}Sr/^{86}Sr$ ratios of the Denison Trough dawsonite cements in sandstones can be explained by the interaction of fluids with detrital K-feldspar. The formation of dawsonite is attributed to elevated CO_2 fugacity and alkalinity in the geochemically more evolved environment at the latest stage of the fluid flow process. Our results indicate that CO_2 has largely been used for carbonate precipitation (mineral trapping) in eastern Australian basins in a temperature range between 100 and 200°C at depths less than 3000m with a significant proportion stored in coal seams as adsorbed molecules on coal since the Mesozoic (adsorption trapping). Gas stable isotopes confirm generation of seconday biogenic methane in CO_2-rich coal seams by reduction of CO_2 that suggests methanogenesis provides an additional sequestration mechanism for CO_2 in coal seams.