

Methane fluxes and turnover in permanent anoxia: *In situ* studies of the Dvurechenskii mud volcano (Black Sea)

A. LICHTSCHLAG¹, J. FELDEN¹, F. WENZHÖFER¹, T. MOHR², T. FESEKER³, A. BOETIUS^{1,4} AND D. DE BEER¹

¹Max Planck Institute for Marine Microbiology, Bremen, Germany; (alichtsc@mpi-bremen.de)

²RCOM, University Bremen, Germany

³Ifremer Centre de Brest, Géosciences Marines, BP 70, F-29280 Plouzané, France

⁴Jacobs University Bremen, Bremen, Germany

Cold seeps are often called oases of life in the deep sea for their rich chemosynthetic communities populating the seafloor. Many typical seep organisms like the giant tubeworms, diverse bivalves and mats of giant sulfide oxidizing bacteria have a considerable influence on the biogeochemistry of methane-laden seafloor e.g. by bioturbation, bioirrigation and by replenishing sulfate to the electronacceptor-limited sediments. Here we investigated the biogeochemistry of a gas-emitting cold seep system in permanently anoxic waters, where animal life is completely absent. At most cold seeps the methane rising from subsurface reservoirs is oxidized anaerobically with sulfate diffusing into the seafloor from the overlying bottom water. Normally the produced sulfide is further oxidized by chemical and microbiological processes with either Fe(III), nitrate or oxygen as terminal electron acceptor. In the Black Sea these electron acceptors are absent below the chemocline, thus the sulfide may be largely exported to the water column.

This study was carried out at the Dvurechenskii mud volcano (DMV, Sorokin Trough) during expedition M72/2 with RV METEOR and ROV QUEST (MARUM, Bremen) in the framework of the EU FP6 integrated project HERMES and the DFG/BMBF GEOTECHNOLOGIEN program MUMM.

The main questions of our investigation were 1) Where are the hotspots of methane emission and turnover at the DMV?, 2) How does the absence of bioturbation affect rates and distribution of anaerobic oxidation of methane?, 3) How does the absence of oxygen and nitrate in the bottom water affect pH gradients and sulfide fluxes?

To answer these questions, we carried out *in situ* microprofiler measurements of H₂S, pH, redox, and temperature along a transect from the center of the mud volcano northwards to the outer rim. Methane-fueled sulfate reduction was measured *in situ* by using the INSINC incubator and methane fluxes were determined with a benthic chamber as well as by concentration measurements in gravity cores and bottom water. Our results show that fluid flow velocity strongly controls methane turnover and export at these anoxic cold seeps, suggesting that the absence of seep fauna reduces the efficiency of the benthic methane filter.

Stable Strontium ($\delta^{88/86}\text{Sr}$) and U-Th systematics of cold-water corals as new proxy for Holocene changes of the Mediterranean outflow

V. LIEBETRAU, A. RÜGGERBERG, J. FIETZKE, A. EISENHAEUER, S. FLÖGEL, P. LINKE AND J. SCHÖNFELD

Leibniz Institute of Marine Sciences, IFM-GEOMAR, Kiel, Germany (vlietbrau@ifm-geomar.de)

This study combines the stable strontium isotope method ($\delta^{88/86}\text{Sr}$) after Fietzke and Eisenhauer (2006) as a potential paleotemperature proxy with MIC-ICP-MS (multi ion counting – inductively coupled plasma – mass spectrometry) U-Th geochronology on cold-water corals from the central Gulf of Cadiz. The sampled reef structure in 1325 m depth on top of the Captain Arutyunov Mud Volcano (MV) consists predominantly of dead *Lophelia pertusa*, accompanied rarely by living solitary corals (*Flabellum sp.*, *Dendrophyllium sp.*).

Potentially recorded environmental influences on these archives are significant water mass changes, e.g. variation of depth and intensity of the Mediterranean Outflow Water (MOW) due to climate changes, time intervals of marine methane emanation (surface-near gas-hydrate occurrence close to the coral site) and the mud volcano activity itself.

Assuming a temperature dependent strontium isotope fractionation during calcium carbonate precipitation temperatures were determined for the living solitary corals, ranging from 9 to 11.5 °C (typical error: $\pm 1^\circ\text{C}$). For comparison, during sampling the bottom water temperature was 8.96 °C and the lower MOW reached from 1075 to 1188 m depth with 10 to 10.5 °C. First U-Th age data reflect slow growth rates of 0.13 to 0.25 mm/year for the solitary corals.

However, the temperature correlation implies the stable strontium approach, which was originally deduced from reef building corals, as suitable for solitary species as well.

For the fossil *Lophelia pertusa* colonies the actual $\delta^{88/86}\text{Sr}$ data set indicates a range from 7.5 to 13 °C with a distinct U-Th age distribution over the last 10 ka, closely correlating with the water depth specific record of lower MOW published by Schönfeld and Zahn (2000). The implication of a lower MOW control on reef formation is supported by coincidence of its actual elevated position with the lack of living *Lophelia pertusa* at the sampling site.

The stable strontium isotope ratio $\delta^{88/86}\text{Sr}$ of biogenic carbonates may serve as a new paleo-temperature proxy for reef-building and solitary deep-sea corals and thus introduce new perspectives in paleoceanography, such as changes in intermediate and deep-sea temperature and ocean circulation.

References

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Schönfeld J. and Zahn R. (2000), *Palaeogeography Palaeoclimatology, Palaeoecology* 159, 85 – 111.