PORE WATER GEOCHEMISTRY OF CH4-RICH MUD VOLCANO SEDIMENTS IN THE EASTERN MEDITERRANEAN SEA: IMPLICATIONS FOR FLUID ORIGIN, THE PRESENCE OF GAS HYDRATE AND BIOGEOCHEMICAL REACTIONS

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Abstract

Pore water geochemical studies were carried out in surface sediments of eastern Mediterranean mud volcanoes to study the following issues:

1 - What is the impact of methane-rich fluid flow for microorganisms and macrobenthic fauna?

2 - What are differences in fluid composition within single mud volcanoes and in different areas?

3 - Is gas hydrate present and what are the conditions of formation?

Keywords: Anaerobic methane oxidation, macrofauna, gas hydrate, fluid flow

Submarine mud volcanoes are frequently found in active continental margins such as the Mediterranean Ridge. They are formed by overpressurized mud in the deep subsurface where methane-loaded fluid flow originates. High methane concentrations in the ascending fluid make gas hydrate formation possible given the required temperature and pressure conditions and create highly adapted forms of life depending on methane as a carbon source.

Mud volcanoes of the Olimpi mud volcanoe field (OMV) and of the Anaximander Mountains (AM) were the subject of a French-Dutch interdisciplinary project. In 1998 direct observations and sampling of sediment and biota were carried out from the French submersible 'Nautile' during 20 dives. In 1999 sampling was carried out by means of box, gravity, and piston coring on-bord of R/V Prof. Logachev. Direct observations revealed heterogeneously distributed occurrence of microbial mats and macrofauna such as clams, mussels, tube worms, sponges, urchins, crabs and fish. Often fields of empty (dead) shells were found. Apart from biota, up to decimeter thick carbonate crusts were found on top of the sediment. On Napoli Dome, a mud volcano located in the OMV, discrete brine water seepage induces creek-like downhill flow ending in brine ponds and lakes.

The most important process with respect to carbon turn-over is anaerobic methane oxidation ($SO_4^{2-} + CH_4 \rightarrow HS^- + HCO_3^- + H_2O$), which has been prooved in the studied sediments by means of organic compound identification (1) and which is also evident from pore water data. SO_4^{2-} typically becomes depleted in the upper meter, which coincides with depletion of upward ascending CH_4. As a result of anaerobic methane oxidation build-ups of HS^- and dissolved inorganic carbon are found in the pore water. The latter leads to supersaturation and precipitation of carbonate which explains the observation of abundant authigenic carbonate.

Pore water distribution of conservative constituents display significant differences for different mud volcanoes: On Napoli dome (OMV) Cl, Na and B always increase with depth in the uppermost sediment and stay constant below. This implies an ascend of brine water enriched in Na and B by a factor of ~10 versus normal sea water which is in agreement with brine water occurrences and composition west of the OMV, Urania and Bannock Brines. In contrast, in mud volcanoes of AM both conservative tracers show sea water concentrations in the uppermost decimeters. Below this zone Na is decreasing whereas B is increasing. Homogeneous sea water-like concentrations of Na, B can only be explained by intensive bioirrigation, presumably by macrofauna which live in symbiosis with CH_4 / HS^- oxidizing bacteria. B enrichment originates here from leaching of detrital sediment under high temperature conditions. The decrease of Na is traditionally explained by the in-situ presence of gas hydrate, which dissociate during core recovery and dilute ambient pore water.

To assess in situ methane concentrations required for the formation of gas hydrate we developed a coupled transport-reation model. In this model we predict the methane depth distribution by setting the methane flux equals to the sulfate flux which is justified by the net reaction of anaerobic methane oxidation (see above) and use the advection velocity derived from fitting conservative constituents (Na, B) with a transport equation accounting for diffusion and advection. Model results from two cores reveal that *in situ* methane concentrations are not high enough for the formation of gas hydrate despite the finding of reduced concentrations of conservative constituents. We interpret this by dehydration of smectite in the deep subsurface serving as fresh water source.

References

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