

**DIFFERENTIATION OF HYDROCARBONS DURING MIGRATION AND GAS  
HYDRATE CRYSTALLIZATION IN SEDIMENTS OF THE AMSTERDAM  
MUD VOLCANO, NORTH EASTERN MEDITERRANEAN SEA**

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Mud volcanoes discharging hydrocarbons are well known from deep-sea areas. They are often accompanied by shallow-buried gas hydrates, which might serve as an important pool of methane and further low-molecular-weight (LMW) hydrocarbons. Although crucial for assessing biogeochemical processes taking place in mud volcano sediments, the abundance and fate of individual hydrocarbons in different gas pools during migration through the upper sediment is generally not well constrained.

Numerous mud volcanoes associated with hydrocarbon seepage are located in deep waters on the north eastern flank of the Mediterranean Ridge (Woodside et al., 1998, Charlou et al., 2003). During a recent expedition with the German RV METEOR (M70-3) and the remotely operated deep-sea vehicle QUEST to the Anaximander Mountains Area, we investigated the *in situ* amounts and fate of LMW hydrocarbons (C<sub>1</sub> to C<sub>6</sub>) brought along by fluids of the Amsterdam Mud Volcano (35:20N; 30:16E; 2,050 m water depth). With respect to *in situ* gas concentrations, autoclave technology, which exclusively preserves ambient pressure and prevents gas losses, was used for sediment and water sample recovery. The main focus was laid on the partitioning of specific hydrocarbons in different sedimentary pools during their migration in the upper sediment layers. Therefore, we measured the abundances and distribution patterns of volatile hydrocarbons in shallow sediments and in gas extracted from near-bottom water samples. For comparison, the hydrocarbon distributions in gas bubbles emanating from the seafloor and in gases released by gas hydrate dissociation were determined.

Side scan sonar surveys and near-bottom video observations revealed seafloor features typical for mud volcanism and hydrocarbon seepage (e.g. circular-shaped morphology, carbonate crusts, seep-associated fauna dominated by tube worms and bivalves). Bubble flares in the water column indicated active gas seepage during the sampling campaign. Sediment samples from the centre of the MV retrieved mud breccia as typical Mud Volcano deposits.

Controlled gas release from pressurized sediment cores retrieved with the Dynamic Autoclave Piston Corer (volumetric capacity 13 L; Abegg et al., submitted) from the centre of

the MV yielded up to 140 L gas per core. Gas chromatographic analyses of sub-samples taken in high-resolution during the incremental degassing procedure showed a strong dominance of methane (up to 98.6 % of C<sub>1</sub> to C<sub>6</sub> hydrocarbons; molar ratio  $R = C_1/(C_2+C_3) = 76.4$ ) in the gas initially released. A strong decline in the ratio during the degassing, with R being as low as 9.5 for gases obtained in the final stage, might be attributed to preferential release from gas pools of different composition. This assumption is supported by results obtained 1) for hydrocarbons released by controlled dissociation of pure gas hydrate pieces ( $R = 15.2$ ) and 2) for gas-hydrate coated bubbles sampled with a newly designed autoclave bubble sampler directly above the seafloor ( $R = 68.9$ ).

Future work applying different methodological approaches (gas isotope chemistry, pore water chemistry, X-ray computed tomography on deep-frozen sediment cores) will give information on type(s) of the source gas, on the distributions of gas hydrates, free gas, and gas dissolved in interstitial water in the sediments, and on internal dynamics of these reservoirs during controlled degassing of pressurized cores. Laboratory experiments are designed to check for adsorption/desorption capacities of the specific sediments for LMW hydrocarbons. Gas hydrate crystal structure(s) will be determined in order to characterize the source gas – hydrate interrelationships at the Amsterdam Mud Volcano. The results are fundamental for an evaluation of hydrocarbon-based biogeochemical processes in shallow sediments at mud volcanoes.

## REFERENCES

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