

ADSORPTION OF GASEOUS HYDROCARBONS TO MARINE SEDIMENTSTobias MOHR¹, Sean SYLVA², Jeff SEEWALD² and Kai-Uwe HINRICHS¹*1. Organic Geochemistry Group, Department of Geosciences, University of Bremen, P.O. 330440, 28334 Bremen, Germany**2. Woods Hole Oceanographic Institution, Marine Chemistry & Geochemistry Department, Mail Stop 4, Woods Hole, MA 02543, USA.*

For constraining reservoirs of low-molecular weight hydrocarbon (HC) gases in marine sediments, it is necessary to assess the amount of sorbed gases. Sorption of HC gases to marine sediments is a well-known phenomenon but has not yet been quantified and mechanistically constrained. The dynamics of gas partitioning between the four gas reservoirs, i.e., aqueous state, as solid clathrate, free gas, and bound to sediment particles by sorptive forces, and their relationship to turnover of HC gases are not understood. Our study seeks to obtain a better understanding of the least explored gas pool, sorbed gas, and to assess its importance in biogeochemical processes.

First, we compared protocols for the extraction of sorbed HC gases and found that a recently introduced technique (Hinrichs et al., 2006) based on leaching of the sediment in 1-N aqueous NaOH resulted in up to an order of magnitude higher yields than obtained from previously applied approaches based on treatments with boiling phosphoric acid (e.g. Whiticar & Suess, 1990; Knies et al., 2004) or autoclaving (Sugimoto et al., 2003). Our observations do not support previous interpretations of sorbed gas as mostly derived from thermogenic sources due to their ¹³C-enrichments relative to dissolved gas (Whiticar & Suess, 1990). Instead, we suggest that previously applied protocols selected for pools of gases that were isotopically enriched relative to bulk sorbed gas. This statement is supported by observations of relatively large variations of isotopic compositions of sub-samples, released in increments from single samples of sediment or clay mineral. The origin of the sorbed gas pool appears to be closely related to that of the other gas pools and is interacting with these through a variety of processes, including biological ones.

The partitioning of methane and other HC-gases between the dissolved and sorbed pools is highly variable. In some occasions, the sorbed pool exceeds the amount of HC-gases dissolved in the pore water by several orders of magnitude. In the deep Japan Trench, sorbed methane is typically more abundant than dissolved methane. Carbon isotopic values of both pools clearly indicate microbially-derived gases ($\delta^{13}\text{C} = -80\text{‰}$ to -70‰). The difference between δ values between the sorbed and dissolved gas phase, $\Delta\delta^{13}\text{C}$ -values range from -8 to +4 ‰ vs. VPDB (Fig. 1). The mechanistic causes of these differences are not yet fully

understood but the current evidence points towards strong interactions of isotopic partitioning of the gas pools by biological sources and sinks in combination with distinct kinetics of certain sorptive sites in clay minerals regarding sorption and desorption.

Likely adsorbents are layered clay minerals such as smectites. This is supported by computational geochemistry (Sposito et al., 1998), the efficiency of the extraction procedure with NaOH, which is likely to cause delamination of layered clay minerals, thus causing release of enclosed gas (cf. Hinrichs et al., 2006), and, most importantly, laboratory experiments with pure clay minerals. For example, in autoclave experiments at 200 bar, we were able to show uptake and subsequent extraction of ~ 43 mmol/kg Na-montmorillonite. These observations support a key role of layered clay mineral as sorbents for HC gases in marine sediments.

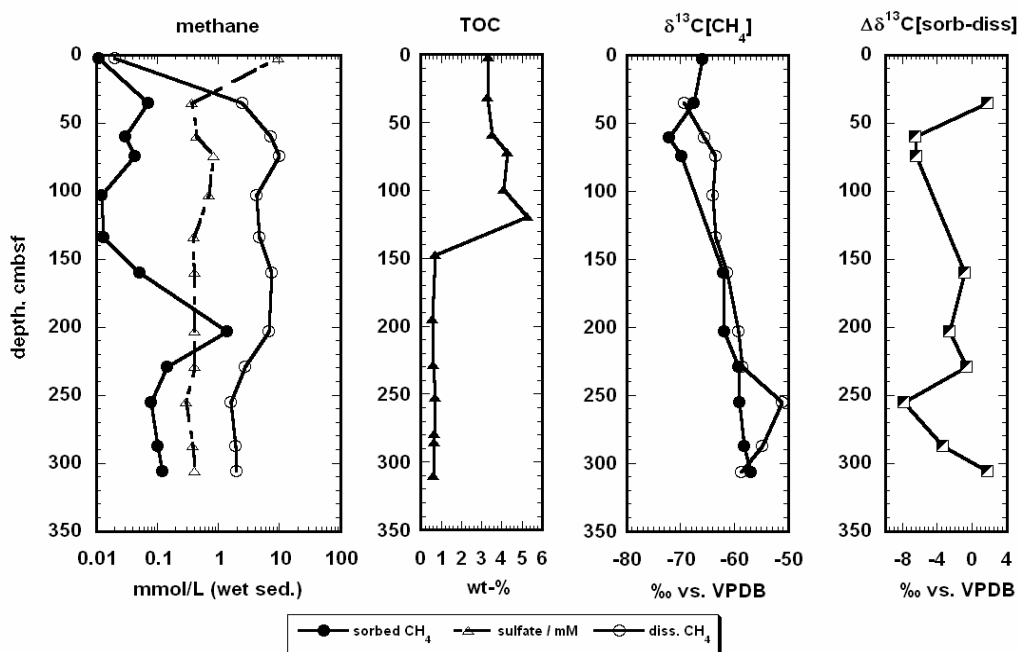


Figure 1. Depth profile of a cold seep sediment core of the Turkish Margin in the SW Black Sea (Trakya, close to Bosphorus outlet, 883 mbsf, BS-340-G, TTR15).

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