

## CARBON ISOTOPIC COMPOSITIONS OF VOLATILE FATTY ACIDS AS PROXIES FOR BIOGEOCHEMICAL PROCESSES IN GAS HYDRATE BEARING SEDIMENTS

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In recent decades, our understanding of biogeochemical processes has benefited enormously from the information encoded in the stable carbon isotopic composition of organic molecules. For low-molecular-weight metabolites,  $\delta^{13}\text{C}$  values are routinely acquired for methane and used to examine details of its production and consumption. Similarly, the carbon isotopic composition of acetate, a ubiquitous intermediate in anaerobic metabolism, is affected by its sinks and sources. However, systematic information on the isotopic composition of acetate and other water-soluble metabolites in natural environments is rare due to analytical obstacles (for references see Heuer et al, 2006). Only the recent development of a new technique for online isotope-ratio-monitoring liquid chromatography/mass spectrometry (irm-LC/MS) (Krummen et al., 2004) has set the stage for routine carbon isotopic analysis of dissolved volatile fatty acids (VFAs). A first systematic irm-LC/MS survey of VFAs in a wide range of natural sediments and sediment incubations has revealed a large variability in the carbon isotopic compositions of acetate, propionate and butyrate with  $\delta^{13}\text{C}$  values ranging from -5‰ to -85‰ vs VPDB (Heuer et al., 2006). Incubation experiments suggest a systematic link between the carbon isotopic composition of the investigated VFAs and the dominant-carbon transforming processes of the sediments, i.e. fermentation, methanogenesis and homoacetogenesis. These latest findings underline the potential of  $\delta^{13}\text{C}$  values of acetate and other VFAs as powerful indicators of biogeochemical processes predominating *in situ* in natural sediments.

In this presentation, we will examine the role of acetate in gas hydrate-bearing sediments. Based on  $\delta^{13}\text{C}$ -values of methane, a large fraction of the methane in marine gas hydrates is thought to result from biogenic sources. However, only little is known about methanogenic processes in the deep marine biosphere, deep pore-water profiles of the potential methane precursor acetate are rare (e.g. Egeberg and Barth, 1998; Wellsbury et al. 2000), and  $\delta^{13}\text{C}$  values of acetate have not been reported for this type of environment, yet. We will show results from carbon isotopic investigations of gas hydrate bearing sediments at the Cascadia Margin, NE Pacific, which were drilled during Integrated Ocean Drilling

Program Expedition 311. We find both concentrations and isotopic compositions of acetate to change with sediment depth (Fig 1). Acetate concentrations rise from  $<5 \mu\text{M}$  at the sediment-water interface to  $670 \mu\text{M}$  at 250 meters below seafloor.  $\delta^{13}\text{C}$  values of acetate increase from  $-35$  to  $-17\text{‰}$  vs VPDB. Given uniform  $\delta^{13}\text{C}$  values of dissolved organic carbon (DOC) close to  $-23\text{‰}$ , the low values of acetate in the top 130 m of the sediment column require either partial production of acetate from a  $^{13}\text{C}$ -depleted pool of precursors such as biomass from methanotrophs or partial production of acetate by  $\text{CO}_2$  reduction (homoacetogenesis). Accordingly, a change in the precursor pool below 130 mbsf or an increasing importance of acetoclastic methanogenesis are plausible processes explaining the increase of  $\delta^{13}\text{C}$  of acetate with depth. The feasibility of the latter process, flow of acetate to methane, is supported by thermodynamic calculations.

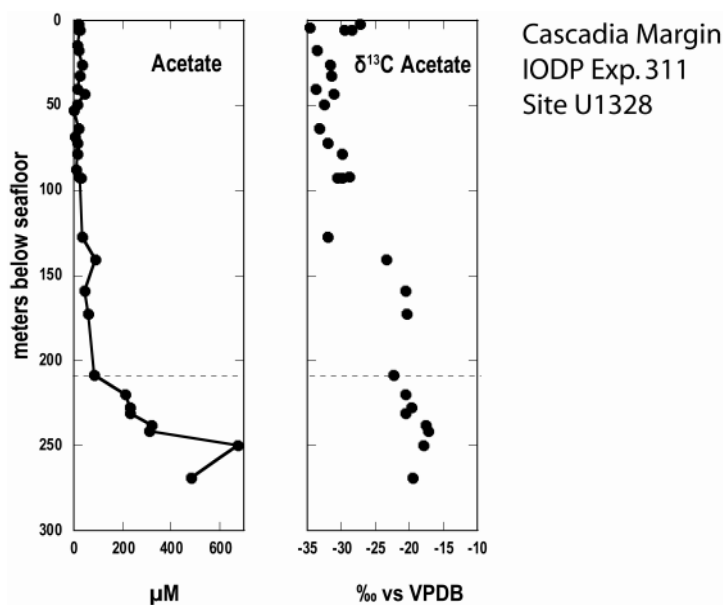


Figure 1. Analysis of pore-water acetate by irm-LC/MS yields quantitative and carbon isotopic data for samples obtained from gas-hydrate bearing sediments at the Cascadia margin, NE Pacific. The dashed line indicates the depth of the bottom simulating reflector and is assumed to represent the base of the gas hydrate stability field.

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