Carbon isotopic compositions of acetate as proxies for biogeochemical processes in gas hydrate bearing sediments

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A large fraction of methane in marine gas hydrates results from biogenic sources, but the processes that generate methane in the deeply buried sediments remain to be elucidated. IODP Expedition 311 drilled a transect across the Cascadia Margin, NE Pacific, to study the distribution and evolution of gas hydrates in an active continental margin. In our post-cruise research, we seek to identify processes and reactants involved in methane formation by compound-specific isotopic analysis (CSIA) of dissolved carbon-bearing compounds such as acetate. So far, deep pore-water profiles of acetate concentration are rare and $\delta^{13}C$ values of acetate are largely lacking due to analytical obstacles.

Our recent survey of a wide range of natural sediments and sediment incubations has revealed a large variability in the carbon isotopic compositions of acetate and incubation experiments suggest a systematic link between the carbon isotopic composition of acetate and the dominant carbon transforming processes of the sediments, i.e., fermentation, methanogenesis and homoacetogenesis (Heuer *et al*., 2006).

At the Cascadia Margin, both concentrations and $\delta^{13}C$ of acetate vary considerably. Acetate concentrations increase from <5 µM at the sediment-water interface to 670 µM at 250 meters below seafloor. $\delta^{13}C$ values of acetate range from -50 to -8‰ vs VPDB. Given uniform $\delta^{13}C$ values of dissolved organic carbon (DOC) close to -23‰, the low values of acetate require either partial production of acetate from a ^{13}C-depleted pool of precursors such as biomass from methanotrophs or partial production of acetate by CO_2 reduction (homoacetogenesis). On the other hand, the high values of $\delta^{13}C$ of acetate in some hydrate-bearing sediment intervals likely point to acetoclastic methanogenesis as an important sink of acetate. CSIA of dissolved organic compounds provides novel information on the molecular-scale processes in deeply buried sediments that lead to formation of methane and ultimately methane hydrate.

Reference

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Biological fractionation of Ca isotopes ($\delta^{44/40}Ca$): A study in Göttingen minipigs

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Calcium is an essential element in human physiology and plays an important role in many processes. Due to its important role Ca concentrations are kept within small limits in the extracellular space. This Ca homeostasis is maintained by three organs, the gastrointestinal tract (input of Ca), the skeleton (store of Ca) and the kidney (output of Ca). Physiological ageing processes and many chronic diseases are associated with disturbances of the calcium metabolism.

In a study at the Federal Research Centre for Nutrition and Food several animal trials with the Göttingen miniature pig for generation of osteopathies have been carried out. The Göttingen miniature pig was chosen for these trials as their physiology is comparable to human physiology (e.g. Scholz-Ahrens *et al.*, 2007). We analyzed food, feces, blood, bone and urine samples of six animals from these trials in order to study the calcium metabolism with respect to stable Ca isotopes and their fractionation.

Feces had $\delta^{44/40}Ca$ values similar to the $\delta^{44/40}Ca$ of the semi-synthetic diet (0.42‰) or exhibit a fractionation which tends to result in lower $\delta^{44/40}Ca$ values in feces. Blood $\delta^{44/40}Ca$ values vary from 0.06‰ to 0.68‰ and are on average 0.68‰ heavier than the bone $\delta^{44/40}Ca$ values (-0.60‰ to -0.03‰) This difference between the $\delta^{44/40}Ca$ values of blood and bone is only half of the difference between soft and mineralized tissue reported by Skulan and DePaolo (1999).

$\delta^{44/40}Ca$ values of urine samples range from 2.05‰ up to 2.68‰ and are approximately 2‰ higher than the corresponding blood $\delta^{44/40}Ca$ values of the same animal. Presumably, the observed fractionation between blood and urine mainly occurs in the kidney This enrichment of heavy Ca in urine may be due to preferential transport of ^{40}Ca by Ca transporters in the renal tubules, by which more than 98% of the calcium of the primary urine is reabsorbed (Hoenderop *et al*. 2005) in a repetitive process.

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