CO_2 injection into submarine, CH_4-hydrate bearing sediments: geochemical implications of a hydrate conversion technology

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With the aim of emission neutral energy production, combined CH_4-hydrate exploitation from and CO_2 storage in marine gas hydrate reservoirs is investigated. Little is known about the geochemistry of hydrates and their host sediments before, during and after production. Results from the recent *Ignik Sikumi* gas hydrate field trial have indicated that the injection of a CO_2-rich fluid into the hydrate reservoir produces mixed hydrates in a slow conversion process. This and the awareness of potential effects of natural and technically induced heterogeneity drives the ambition to understand hydrate conversion on the pore scale.

Our recent studies suggest that the injection of heated, supercritical CO_2 is beneficial for both CH_4 production and CO_2 retention at different hydrate reservoir temperatures ranging from 2 °C to 10 °C [1]. Yet, our findings can only be explained by the induction of a variety of spatial and temporal processes which result in substantial bulk heterogeneity, characterized by formation of mixed CO_2-CH_4-hydrates, hold-up of hydrate-derived CH_4 gas in pore spaces, permeability changes and temperature dependent CO_2-channeling. Interestingly, while CH_4 production and CO_2 retention yields varied considerably between different experiments, water production was largely similar. Using online IR-based sensor technology and Raman spectroscopy, distinct intervals of water and gas production could be identified, which suggest, that the slow formation of CO_2- or mixed CO_2-CH_4-hydrates was responsible for increased CH_4 production yields. Additional Magnetic Resonance Imaging (MRI) experiments were performed to visualize the intrusion of liquid CO_2 into the sediment/hydrate matrix.

It is a central objective of our studies to improve available transport-reaction models and strengthen the link between pore scale and reservoir modelling, by finding empirical relations suitable for implementation in current numerical simulators.

[1] Deusner *et al.*. (2012) Energies 5, 2112-2140

Isotopic and stoichiometric constraints on marine denitrification from a global inverse circulation model

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A major impediment to understanding long-term changes in the marine nitrogen (N) cycle is the persistent uncertainty about the rates, distribution, and sensitivity of its largest fluxes in the modern ocean. We use a global ocean circulation model to obtain the first 3-dimensional estimate of marine denitrification rates that is maximally consistent with available observations of nitrate deficits and the nitrogen isotope ratio of oceanic nitrate. We find a global rate of marine denitrification in suboxic waters and sediments of 120–240 TgN/yr, which is lower than many other recent estimates. The difference stems from the ability to represent the spatial structure of suboxic zones, where denitrification rates of 50–77 TgN/yr result in up to 50% depletion of nitrate. This depletion reduces the effect of local isotopic enrichment on the rest of the ocean, allowing the N isotope ratio of oceanic nitrate to be achieved with a sedimentary denitrification rate about 1.3–2.3 times that of suboxic zones. This balance of N losses between sediments and suboxic zones is shown to obey a simple relationship between isotope fractionation and the degree of nitrate consumption in the core of the suboxic zones. The global denitrification rates derived here suggest that the marine nitrogen budget is likely close to balanced.

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