



Modelling carbon isotope composition of dissolved inorganic carbon and methane in marine porewaters

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Carbon isotope compositions of dissolved inorganic carbon (DIC) and methane (CH₄) in marine sedimentary porewaters at near surface temperatures show extremely large variation in apparent fractionation covering a range from -100 ‰ to +30 ‰. This fractionation is essentially the result of microbial activity, but the mechanisms and factors controlling this fractionation are still incompletely understood. This study provides a reaction transport model approach to evaluate the effects of the most important processes and factors on carbon isotope distribution with the goal to better understand carbon isotope distribution in modern sediment porewaters and in the geological record.

Our model results show that kinetic fractionation during methanogenesis, both through the acetoclastic and autotrophic pathways, results in a nearly symmetrical distribution of $\delta^{13}\text{C}$ values in DIC and CH₄ with respect to the isotope value of buried organic matter. An increased fractionation factor during methanogenesis leads to a larger difference between $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{CH}_4}$. Near the sulphate methane transition zone, DIC is more depleted in ¹³C due to diffusive mixing with DIC produced by anaerobic oxidation of methane (AOM) and organoclastic sulphate reduction. The model also shows that an upward decrease in $\delta^{13}\text{C}_{\text{CH}_4}$ near the SMT can only be caused by equilibrium fractionation during AOM including a backward “leakage” of carbon from DIC to CH₄ through the enzymatic pathway. However, this effect of reversibility has no influence on the DIC pool as long as methane is completely consumed at the SMT. Only a release of methane at the sediment-water interface, due to a fraction of the methane escaping re-oxidation, results in a small shift towards more positive $\delta^{13}\text{C}_{\text{DIC}}$ values. Methane escape at the SMT is possible if either the methane flux is too high to be entirely oxidized by AOM, or if bubbles of methane gas by-pass the sulphate reduction zone and escape episodically into the water column. A small but significant isotope effect is also caused by differential diffusion of the ¹²C and ¹³C isotopes of CH₄ leading to somewhat more positive $\delta^{13}\text{C}_{\text{CH}_4}$ values, while DIC remains unaffected by this process.

The consideration of all these effects allows a relatively good reproduction of $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{CH}_4}$ profiles in marine sediments in diffusive systems. However, the model cannot reproduce profiles measured in seep environments, where CH₄ and DIC profiles are perturbed by upward advecting, possibly thermogenic methane from greater depth. The model is now available to be applied for non-steady state systems, which ultimately will help to understand past dynamics of $\delta^{13}\text{C}$ compositions and their diagenetic records as a result of changing microbial activity.