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Explaining sulfate-driven isotope effects in anaerobic oxidation of methane using a metabolic-isotopic model

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Anaerobic oxidation of methane (AOM) by archaea coupled to sulfate reduction in partner bacteria is prevalent in marine sediments. AOM activity in marine sediments usually peaks at the sulfate-methane interface (SMI), where methane from the deeper sediments meets sulfate diffusing from the overlying seawater. According to established isotope systematics, methane remaining from partial oxidation should be enriched in ^{13}C. However, in these SMIs methane $\delta^{13}C$ values often decrease, a pattern that was thought to be caused by methanogenesis. Alternatively, sulfate-limiting conditions are suggested to decrease methane $\delta^{13}C$ values without methanogenic activity, due to closer-to-equilibrium conditions in the AOM pathway.

We developed a quantitative model of AOM to underpin the metabolic mechanisms that generate the carbon isotope effect and the accompanying hydrogen isotope effect in low- and high-sulfate conditions. We calibrated the model with concentration and isotope data from a sediment-free enrichment culture of a thermophilic sulfate-dependent AOM consortium (ANME-1 and a partner sulfate reducing bacterium), which is ideal to investigate the effects of sulfate availability on methane isotope compositions. Under sulfate-replete conditions (10 mM) methane $\delta^{13}C$ and $\delta^{2}H$ values increased as expected, while under sulfate limitation (<1 mM) methane $\delta^{13}C$ values decreased and $\delta^{2}H$ values plateaued. Moreover, ^{14}C-radiotracer labeling experiments revealed that the DIC–methane reversibility did not exceed 15% even under sulfate limitation, similar to previous experiments and far from complete DIC–methane reversibility. We used these experimental constraints to find a unique combination of reaction-specific reversibilities in the AOM pathway that yielded an optimal fit.

The model reveals that in low-sulfate conditions, effective isotopic exchange (i.e., high reversibility) between the intracellular metabolite formylmethanofuran and methane has only a small effect on the net isotopic exchange between DIC and methane, but a major effect on methane $\delta^{13}C$ and $\delta^{2}H$ values. Hence, large variations in methane $\delta^{13}C$ values do not require high DIC–methane reversibility, which would imply near-equilibrium AOM activity, contrary to observations from SMIs. Our results highlight that negative methane $\delta^{13}C$ excursions in SMIs may not be used as evidence for concurrent methanogenesis and AOM, and provide predictions for methane $\delta^{2}H$ values in future explorations of AOM.