



## Isotope fractionation and isotope decoupling during nitrate reduction in marine sediments

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In summer 2010, we sampled marine sediments in the Skagerrak, covering a gradient of reactivity, oxygen consumption, and manganese concentration in the sediment. Along this gradient, we aimed to evaluate links between nitrogen cycling and sediment properties. The focus of the study was the interplay of nitrate and nitrite reduction rates and concomitant nitrate and nitrite isotope changes in sediment incubations.

As expected, nitrate reduction was fastest in sediments with highest sediment reactivity and oxygen consumption. At the shallower sampling sites, denitrification was the main removal pathway of nitrate and nitrite, but acetylene inhibition experiments pointed towards significant importance of anammox at the deepest site in the Skagerrak.

The N-isotope of denitrification effect varied with depth, with stronger N-isotope fractionation at deeper, and less reactive, sites, and ranged from -12 to -16‰. At the deepest site in the Skagerrak, anammox was the dominant N<sub>2</sub> production pathway. For this site, we calculated the intrinsic isotope effect of anammox in marine sediments, and found that it is ~-15‰, which is in accordance with recent culture studies.

The isotope effect of oxygen, however, was not consistent pattern along the gradient of sediment reactivity. The oxygen isotope effect of nitrate reduction was entirely decoupled from the nitrogen isotope effect. Surprisingly, this variability in oxygen isotope fractionation was not linked to the occurrence of anammox, but rather to intermediate nitrite accumulation in the anoxic incubations. Consequently, the ratio of  $^{18}\epsilon / ^{15}\epsilon$  was highly variable in all sediments we investigated.

We presume that such decoupling of oxygen and nitrogen isotopes is due to anoxic nitrite oxidation, which rises in turn with nitrite accumulation in the sediment incubations. These findings suggest that the ratio of  $^{18}\epsilon / ^{15}\epsilon$  in marine environments is highly flexible, and might, especially in regions with considerable nitrite accumulation, not be a reliable indicator of nitrogen turnover processes in anoxic environments.