

## 4.1.14

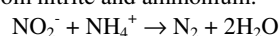
**Anammox and the marine N cycle**

B. THAMDRUP<sup>1</sup>, T. DALSGAARD<sup>2</sup>, M.M. JENSEN<sup>1</sup>  
AND J. PETERSEN<sup>1</sup>

<sup>1</sup>DCESS, Institute of Biology, University of Southern Denmark, Campusvej 55, DK-5230 Odense M (bot@biology.sdu.dk; mmj@biology.sdu.dk)

<sup>2</sup>National Environmental Research Institute, Vejlssøvej 25, DK-8600 Silkeborg, Denmark (tda@dmu.dk)

Anaerobic ammonium oxidation coupled to the reduction of nitrate via nitrite was recently demonstrated to be a sink for fixed N and source of N<sub>2</sub> in both marine sediments and anoxic water columns [1,2]. During the process, N<sub>2</sub> forms through the pairing of N from nitrite and ammonium:



This stoichiometry, as well as physiological characteristics, strongly indicate that the reaction is due to the bacterial anammox process.

The anammox process may contribute significantly to marine N budgets, with potential consequences also for C cycling. With the aim of determining the role of anammox in the marine N cycle, we have explored the rates and regulation of the process in both marine sediments and anoxic water columns.

In a compilation of results from sediments, the contribution of anammox to N<sub>2</sub> production (the fraction of N<sub>2</sub> not formed through denitrification) varied from < 5% in shallow coastal sediments to 70% in a continental basin, and with typical values in open-water continental sediments of 20 – 30%. This variation may be related to competition with denitrifiers for nitrite, though factors controlling such competition are not clear.

In the chemocline of the euxinic Mariager Fjord, Denmark, anammox was not detected while denitrification occurred at high rates and appeared to be coupled to sulfide oxidation. By contrast, in the anoxic basin of Golfo Dulce, Costa Rica, anammox contributions of 20 – 50% measured in spring 2003, reproduced earlier measurements from November 2001 [2]. Rates of both denitrification and anammox were almost 10-fold lower in 2003 than 2001. Suggested intermediates in the anammox process, hydrazine and hydroxylamine, were not detected in the water column, and additions of these species had no effect on anammox rates. Our observations suggest that in water columns, anammox is particularly important in anoxic, non-sulfidic environments, as found in the oceanic oxygen minimum zones, which supports an important role of the process in the marine N cycle.

**References**

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## 4.1.15

**Abiotic Zn isotope fractionations associated with ZnS precipitation**

C. ARCHER<sup>1</sup>, D. VANCE<sup>2</sup> AND I. BUTLER<sup>3</sup>

<sup>1</sup>Department of Geology, Royal Holloway University of London, United Kingdom (c.archer@bristol.ac.uk)

<sup>2</sup>Department of Earth Sciences, University of Bristol, United Kingdom (d.vance@bristol.ac.uk)

<sup>3</sup>Department of Earth Sciences, Cardiff University, United Kingdom (butler@earth.cf.ac.uk)

Due to analytical advances, the field of transition metal isotope research has grown rapidly over recent years. Though an early aspiration was that the isotope geochemistry of the transition metals could elucidate biogeochemical processes, these systems have since been demonstrated to undergo both biotic and abiotic fractionations [1,2]. Thus a detailed understanding of the mechanisms responsible for the isotope fractionation is critical to the successful use of the transition metals in biogeochemistry. Here we report Zn isotope data for preliminary ZnS precipitation experiments undertaken in the absence of biology.

ZnS was precipitated in an anoxic environment at room temperature and allowed to equilibrate for a period of 0 to 168 hours. The residual dissolved Zn was also collected. Both precipitates and residual Zn were chemically purified [3] before Zn isotope compositions were measured using a ThermoFinnigan Neptune MC-ICPMS. Data are presented using the usual delta notation.  $\delta^{66}\text{Zn}$  of the Zn precipitate was determined to be  $-0.36 \pm 0.09\%$ , relative to the Zn source material and this fractionation was independent of the equilibration time. The residual dissolved Zn showed the expected small positive fractionation. The data suggest a kinetic fractionation of about  $-0.36\%$  and the constancy of the fractionation with time suggests that equilibration is slow.

These data indicate that small reservoirs may become depleted in lighter isotopes through inorganic precipitation of ZnS, resulting in reservoirs of relatively heavy Zn. Our recent Fe-Zn dataset for Archean microbial sulphides [4] will be discussed in the context of these new experiments. These new experiments suggest that the Archean microbial dataset can be explained in terms of mixing between two fluids of distinct isotope composition [5] and that the Zn data do not by themselves require a biological mechanism.

**References**

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