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Influence of diagenesis on sedimentary $\delta^{15}N$ in the Arabian Sea over the last 130 kyr

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ABSTRACT

Sedimentary $\delta^{15}N$ records are valuable archives of ocean history but they are often modified during early diagenesis. Here we quantify the effect of early diagenetic enrichment on sedimentary N-isotope composition in order to obtain the pristine signal of reactive N assimilated in the euphotic zone. This is possible by using paired data of $\delta^{15}N$ and amino acid composition of sediment samples, which can be applied to estimate the degree of organic matter degradation. We determined $\delta^{15}N$ and amino acid composition in coeval sediments from Ocean Drilling Program (ODP) Hole 772 B in the central Arabian Sea and from Hole 724 C situated on the Oman Margin in the western Arabian Sea coastal upwelling area. The records span the last 130 kyr and include two glacial–interglacial cycles. These new data are used in conjunction with data available for surface sediments that cover a wide range of organic matter degradation states, and with other cores from the northern and eastern Arabian Sea to explore spatial variations in the isotopic signal. In order to reconstruct pristine N values we apply the relationship between organic matter degradation and ^{15}N enrichment in surface sediments to correct the core records for early diagenetic enrichment. Reconstructed $\delta^{15}N$ values suggest a significant role of N_2-fixation during glacial stages. An evaluation of two preservation indices based on amino acid composition (Reactivity Index, RI; Jennerjahn and Ittekkot, 1997; and the Degradation Index, DI; Dauwe et al., 1999) in both recent sediments and core samples suggests that the RI is more suitable than the DI in correcting Arabian Sea $\delta^{15}N$ records for early diagenetic enrichment.

1. Introduction

The isotope ratio $^{15}N/^{14}N$ in sediment records, expressed as $\delta^{15}N$, is a commonly used proxy to reconstruct changes in the oceanic nitrogen cycle and to evaluate past ocean productivity (Farrell et al., 1995; Ganeshram et al., 2002; Altabet, 2007). The $\delta^{15}N$ of sediments reflects nitrogen sources (dissolved inorganic nitrogen, DIN) (Sweeney and Kaplan, 1980), as well as transformation processes in the ocean that cause isotopic fractionation during cycling of nitrogen (Altabet, 2006). Nitrate—the major DIN species—has an average $\delta^{15}N$ value of about 5.0 ± 0.5‰ in deep waters of the modern global ocean (Sigman et al., 2000), which may have been different in the geological past in response to different sources and sink terms (Brandes and Devol, 2002; Deutsch et al., 2004) but which is supposed to have been stable during the past 140 kyr at least in the Western Pacific (Kienast, 2000). Nitrate in modern intermediate water masses has more variable isotopic signatures than the deep reservoir which can be due to denitrification in oxygen-depleted subsurface waters that enriches the residual nitrate in ^{15}N up to above 15‰ (e.g., Naqvi et al., 1998; Voss et al., 2001; Thunell et al., 2004) or to the more recently discovered anammox process that probably also enriches residual $^{15}NO_3^-$ (Dalsgaard et al., 2003; Ward et al., 2009). Assimilation of such an enriched source entering the euphotic zone leads to $\delta^{15}N$ values of particulate organic matter and sediments far above 5‰ (Naqvi et al., 1998; Altabet et al., 1999b; Voss et al., 2001). Isotopically depleted $\delta^{15}N$ values, on the other hand, often occur in sediments with a strong imprint of relatively pristine terrestrial nitrogen supply (Gaye-Haake et al., 2005; Voss et al., 2005) or in areas of N_2-fixation, which regionally or seasonally introduces depleted $\delta^{15}N$ that has the isotopic signal of air (~0‰; Mariotti, 1984; Karl et al., 2002).

Isotopic fractionation during biological DIN uptake also has an effect on $\delta^{15}N$ of sediments. Lateral gradients of $\delta^{15}N$ in particulate N assimilated from an isotopically homogeneous DIN source are caused by "Rayleigh"-type fractionation during progressive DIN uptake by phytoplankton. The initial products are isotopically depleted over the nitrate pool, whereas later products are enriched over the original substrate (Altabet and Francois, 1994). This process can explain increases of $\delta^{15}N$ in sediments with increasing distance from nitrate sources such as river mouths and upwelling areas (Holmes et al., 1997; Pichevin et al., 2005). Incomplete nitrate utilization also has been invoked to explain varying $\delta^{15}N$ in sedimentary archives (Calvert et al., 1992; Farrell et al., 1995).

Due to the short residence time of nitrogen in the ocean, the nitrogen cycle responds to perturbations on very short time-scales (Tyrrell, 1999; Deutsch et al., 2004). Variations of $\delta^{15}N$ values in late Quaternary sediment records of the Arabian Sea have been interpreted as signals of a response of the nitrogen cycle to climatic oscillations. Climatic changes led to changes in ocean circulation and induce changes in denitrification rates, assimilation rates, nutrient

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limitations, or nitrogen fixation (Suthhof et al., 2001; Altabet et al., 2002; Ganeshram et al., 2002).

However, quantitative reconstructions of the global or regional N-cycles from geological records are generally hampered by early diagenetic overprinting of the original $^{15}N/^{14}N$ ratio. Enrichment in $\delta^{15}N$ by 3–5‰ from particles in the water column to surface sediments have been observed in open ocean sediments (Francois et al., 1992; Francois et al., 1997; Gaye-Haake et al., 2005; Möbius et al., 2010) and have been related to the intensity of degradation as reflected in the reactivity of amino acid (AA) mixtures in sediments (Gaye-Haake et al., 2005; Möbius et al., 2010). Although exact mechanisms remain unknown, kinetic isotope fractionation during protein hydrolysis (Bada et al., 1989; Silfer et al., 1992) and deamination (Macko and Estep, 1984), resulting in the preferential loss of ^{15}N depleted compounds during organic matter (OM) degradation, very likely causes this enrichment.

Decomposition of particulate OM in aquatic environments follows different pathways and occurs in various steps. The main controlling factor is oxygen exposure time (Hartnett et al., 1998) which integrates water column oxygenation, duration of particle sinking as a consequence of water depth and particle size as well as the sealing efficiency driven by sedimentation rates (e.g., Müller and Suess, 1979) that influence the residence time of OM at the sediment water interface. In contrast, sedimentary degradation after burial in the sediment is mediated by other microbial assemblages/communities than in the water column and, depending on the depth of burial and sequestration time, by kinetic/thermal decay ending in katagenesis (e.g., Tissot and Welte, 1978). Indices of organic matter quality derived from AA composition, such as the Reactivity Index RI (Jennerjahn and Ittekkot, 1997) and the Degradation Index DI (Dauwe et al., 1999), are sensitive to degradation of OM in the water column and at the sediment water interface and have often been used to estimate organic matter quality (e.g., Unger et al., 2005; Kaiser and Benner, 2009); the extent to which they are overprinted by late-stage diagenesis upon burial during several thousand years after sedimentation has not been studied.

Our aim is to quantify diagenetic influences on sedimentary $\delta^{15}N$. We investigate surface sediments that were deposited in a wide range of water depths and oxygen contents in bottom waters, and sediment cores with variable sedimentation rates over the last 130 kyr from the Arabian Sea. The main goal of our study is to quantify potential influences on sedimentary $\delta^{15}N$ other than source nitrate $\delta^{15}N$ composition to permit an unbiased reconstruction of nitrate isotopic composition in this key area of the global N-cycle (Altabet et al., 2002). For this we produced paired data of $\delta^{15}N$ and of indices of organic matter degradation (Cowie and Hedges, 1992; Jennerjahn and Ittekkot, 1997; Dauwe and Middelburg, 1998; Dauwe et al., 1999). The suitability of the two indices in studies of OM degradation over geological periods is tested by statistical data treatment on amino acid composition in samples from ODP cores 722 B and 724 C.

2. Study sites

The data set of 46 surface sediments from the Arabian Sea north of 15° N and deeper than 250 m water depth published by Gaye-Haake et al. (2005) is our basis for estimating the effects of water depth and bottom-water oxygen contents on the degradation of both amino acids and $\delta^{15}N$. Oxygen contents in deep waters were interpolated for the sampling sites from the climatology of Gouretski and Koltermann (2004).

New data are presented from 2 Ocean Drilling Program (ODP) sites (722 B and 724 C) in the western Arabian Sea; additional core data are from cores 111 KL, NAST and EAST in the northern and central Arabian Sea (Suthhof et al., 2001; Ivanova et al., 2003) (Fig. 1 and Table 1). Site 722 is located on the Owen Ridge at a water depth of 2028 m (16°37′ N; 059°48′E), i.e. below the oxygen minimum zone of the Arabian Sea. Due to low detrital and biogenic particle fluxes in this offshore setting, the mass sediment accumulation rates (MAR) calculated from linear sedimentation rates (based on the age model and on determinations of dry-bulk densities given in Prell et al. (1989)) on the Owen Ridge are lower than at the Oman margin site 724. Site 724 is located on the upper slope of the Oman margin at a water depth of about 600 m (18°17′N; 057°28′E), i.e. within the oxygen minimum layer. Sediments at site 724 have higher organic carbon contents as well as higher accumulation rates compared to those at site 722. Age models for Holes 722 B and 724 C are based on oxygen isotope stratigraphies

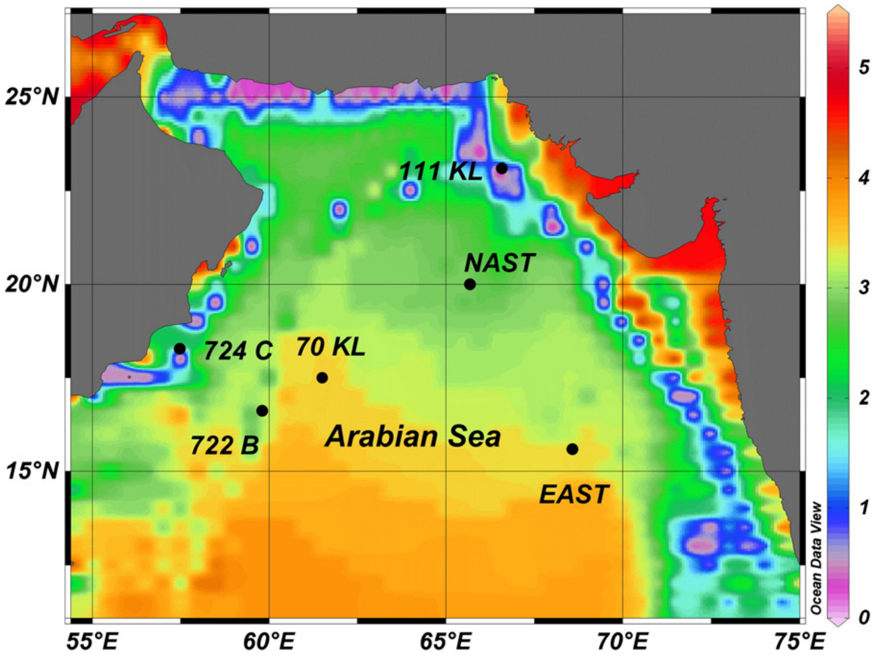

Fig. 1. Oxygen concentrations (ml/l) in bottom water of the Arabian Sea (Gouretski and Koltermann, 2004) and locations of sites referred to in the text. Oxygen concentrations are lowest where the oxygen minimum zone impinges on the continental slope. Patchy patterns result from coarse data resolution. This map is produced by using Ocean Data View (Schlitzer, 2011).