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Separating biogeochemical cycling of neodymium from water mass mixing in the Eastern North Atlantic

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ABSTRACT

The radiogenic neodymium (Nd) isotope ratio $^{143}Nd/^{144}Nd$ (expressed in ε_{Nd}) is being used as a tracer in paleo and modern ocean circulation. However, the mechanisms controlling input, distribution, and internal cycling are far from understood. For example, globally, Nd concentration ([Nd]) commonly follows patterns of nutrient tracers, generally increasing with depth below the thermocline, while ε_{Nd}, tends to reflect the water masses, which has often been referred to as the 'Nd-paradox'. Here we present dissolved Nd isotopes and concentrations at unprecedented vertical and spatial resolution from the eastern part of the US GEOTRACES North Atlantic Zonal Transect (Gulf of Cadiz – Mauritanian Shelf – Cape Verde Islands).

The [Nd] of all samples ranges from 12.3 to 36.7 pmol/kg, with lowest [Nd] usually found within the layer of highest chlorophyll-a levels (chl-max), suggesting removal through scavenging. The Nd isotope compositions range between $\varepsilon_{Nd} = -13.4$ and -9.9, with lower values at the surface within the extension of the Saharan dust plume and a benthic nepheloid layer (BNL). Less negative values are found in oligotrophic surface waters, Mediterranean Outflow Water (MOW), and near the Cape Verde Islands. Overall, water mass mixing derived from ε_{Nd} is best visible at the Strait of Gibraltar, where MOW enters the Atlantic Ocean. Most of the sub-thermocline ε_{Nd} varies within a small range with poor water mass distinction due to the dominance of North Atlantic Deep Water. High surface [Nd] associated with more negative ε_{Nd} is interpreted to be the result of dust deposition and dissolution. Local [Nd] maxima with no apparent change in ε_{Nd} compared to ambient seawater, observed within a zone of minimum oxygen concentration (OMZ) at ~500 m depth off Mauritania, suggest minor input of lithogenic Nd but a rather high contribution through desorption of previously scavenged Nd. That is, Saharan dust in this area has only a minor influence on the isotope composition of water below the uppermost surface layer. The low ε_{Nd} values and elevated [Nd] within the BNL on the other hand indicate release from detrital material. Our new high-resolution dataset gives valuable insights into the Nd distribution near continental margins, influenced by high atmospheric inputs and changing oxygen conditions. We show how vertical and lateral processes overlap to produce the observed Nd distribution, bringing us forward in understanding the Nd-paradox.

1. Introduction

1.1. Neodymium in seawater

The radiogenic neodymium (Nd) isotope ratio $^{143}Nd/^{144}Nd$ (expressed in $\varepsilon_{Nd} = [(^{143}Nd/^{144}Nd)_{sample}/(^{143}Nd/^{144}Nd)_{CHUR} - 1] \times 10^4$ with CHUR = 0.512638 and referring to a 'CHondritic Uniform Reservoir', Jacobsen and Wasserburg, 1980) is increasingly being used as a tracer in paleo- and modern ocean circulation (e.g. Frank,

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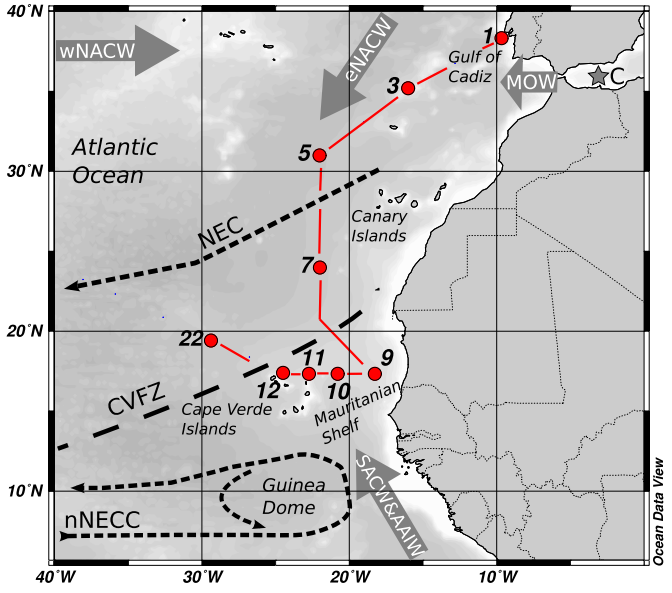

Fig. 1. Station locations from this study (red circles): Stations USGT10-01 to -12 from cruise KN199-4, station USGT11-22 from cruise KN204B. Station C (gray star) from Tachikawa et al. (2004). Dotted arrows and line indicate the main central water currents and position of the Cape Verde Frontal Zone (CVFZ) after Stramma et al. (2005), respectively. Also illustrated are the flow paths of main central and intermediate water masses in the study area: Mediterranean Outflow Water (MOW) eastern and western North Atlantic Central Water (e/wNACW), South Atlantic Central Water (SACW), and Antarctic Intermediate Water (AAIW).

2002; Goldstein and Hemming, 2003; Jeandel, 1993; Lacan and Jeandel, 2005; Pahnke et al., 2008; Piepgras and Wasserburg, 1982; Piotrowski et al., 2005; Rutberg et al., 2000). However, the mechanisms controlling input, distribution and internal cycling are not well understood. Globally, the commonly observed decoupling of concentration ([Nd]) and ε_{Nd}, often referred to as the Nd-paradox, reflects a fundamental lack of understanding of its sources and sinks in the oceans. With the effort of the GEOTRACES program, a steadily growing dataset of modern Nd isotopes and concentrations in seawater is being established. Also on this basis, extensive modeling studies have been realized to better understand processes governing the Nd isotope system in the marine environment (Arsouze et al., 2009, 2007; Jones et al., 2008; Rempfer et al., 2011; Siddall et al., 2008). Improved analytical procedures now permit the analysis of smaller sample sizes, permitting increased spatial resolution and detailed studies of internal cycling processes governing Nd isotope and [Nd] distributions in the ocean. Processes near continental margins, in oxygen minimum zones (OMZ), in nepheloid layers, and in locations where atmospheric inputs are high, need to be studied in great detail in order to understand the Nd cycling in seawater.

Here we present Nd isotope and concentration data along a meridional transect from the Gulf of Cadiz (Spain) to the Cape Verde Islands and a zonal transect along the Mauritanian Shelf (Mauritania) and the Cape Verde Islands at unprecedented vertical and spatial resolution (Fig. 1). The aim of this study is to evaluate the geochemical cycling of Nd at a location dominated by elevated productivity, low oxygen concentrations, high atmospheric inputs, and lateral mixing of water masses from the Mediterranean Sea and the Atlantic Ocean.

1.2. Study area and hydrography

The study area extends from the Gulf of Cadiz in the north to the Mauritanian Shelf in the south, covering the Canary and the Cape Verde Basins (Fig. 1). Seasonal dust storms form a corridor of the Sahara dust plume between roughly 10°N and 30°N (Mahowald et al., 2005). About 140–260 Tg yr^{-1} of Saharan dust are deposited in the North Atlantic Ocean with the highest atmospheric load between May and August (Engelstaedter et al., 2006; Goudie and Middleton, 2001; Jaenicke and Schütz, 1978).

Mediterranean Outflow Water (MOW) enters the Atlantic Ocean through the Strait of Gibraltar and mixes with Eastern North Atlantic Central Water (ENACW, 100–700 m) from the north and Antarctic Intermediate Water (AAIW) from the south between 800 and 1300 m (Louarn and Morin, 2011; Price et al., 1993; Rhein and Hinrichsen, 1993). Western NACW enters the study area via the Gulf Stream System from the West Atlantic (Emery and Meincke, 1986). Another water mass in the upper water column entering the study area from the south is South Atlantic Central Water (SACW, upper 500 m), which shares the same density range as ENACW. These central waters meet at the Cape Verde Frontal Zone (CVFZ, e.g. Stramma and Schott, 1999). Between 1500 m and 3500 m, mainly Upper and Classical Labrador Sea Water (ULSW, CLSW) form the upper North Atlantic Deep Water (NADW), whereas below, Iceland Scotland Overflow Water forms the lower NADW (e.g. Jenkins et al., 2014; Smethie et al., 2007). Antarctic sourced northward flowing bottom water enters the deeper parts of the eastern Atlantic basin, but is only marginally present (Jenkins et al., 2014).

West of Mauritania at 200 to 400 m, the northward turning North Equatorial Counter Current (nNECC) from the West Atlantic forms an upwelling area, the Guinea Dome. The nNECC is the major oxygen supply for the otherwise poorly ventilated central waters in this region (Stramma et al., 2005). Waters from north of the CVFZ are carried southward via the Canary Current around the Canary Islands. This current band becomes the North Equatorial Current (NEC, upper 400 m) when it turns southwestward and leaves the African continent. According to Stramma et al. (2005), due to low exchange between NEC and nNECC, central waters can re-circulate several years within the Guinea Dome leading to poor ventilation. Together with the high productivity and regeneration of organic matter, this forms an oxygen minimum zone (OMZ) with O_2-levels as low as 40 µmol/kg between 400 and 600 m water depth (Brandt et al., 2010; Stramma et al., 2008).

2. Methodology

2.1. Onboard procedure

The samples were collected along the cruise transects of KN199-4 (October to December 2010) and KN204B (November to December 2011) at 9 stations (Fig. 1). A detailed description of the sampling procedure and equipment can be found in Pahnke et al. (2012). Briefly, samples were collected from 10-L standard General Oceanics Niskin bottles with 0.25 mm thick nylon-coated stainless steel springs, Viton O-rings at the end caps and spigots, and mounted on a 24-position powder-coated stainless-steel rosette frame. Seawater was filtered directly from the Niskin bottles through AcroPak500 (0.8/0.45 µm) filter cartridges, which were re-used at each station for the same depth and flushed with seawater prior to sample collection into acid-cleaned LDPE containers. From each bottle, a ~4-L aliquot was collected for Nd isotopes and concentrations. After collection, the samples were acidified to pH $<$ 2 using ultra-clean 6N hydrochloric acid and stored for further processing in the home laboratory. At each station, one 4-L container previously filled with 18.2 MΩ cm water (Millipore) at Lamont–Doherty Earth Observatory (LDEO) was acidified and stored to estimate a conservative procedural blank. The resulting blanks ranged between 30 and 100 pg Nd, which is less than 1.5% of the smallest sample size of 8 ng Nd. No blank correction was applied.