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Towards explaining the Nd paradox using reversible scavenging in an ocean general circulation model

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ABSTRACT

The isotopic composition of the rare earth element neodymium (Nd) has the potential to serve as water-mass tracer, because it is naturally tagged by continental sources with distinct ages and lithologies. However, in order to understand the limitations of this approach we need to know more about the physical and biogeochemical processes controlling the distribution of Nd in the modern ocean. For example, Nd isotope ratios behave quasi-conservatively, while concentrations in the water column generally increase with depth, showing a broadly nutrient-like behaviour. We define this decoupling of Nd concentrations and isotopic compositions as the “Nd paradox”. For the first time we model Nd concentrations and isotopic compositions simultaneously and address the hypothesis that the Nd paradox can be explained by a combination of lateral advection and reversible scavenging. We impose a reversible-scavenging model of Nd removal from the ocean on the ocean circulation fields from the MIT general circulation model using the transport matrix method. We conclude that reversible scavenging is an active and important component in the cycling of Nd in the ocean. In the absence of an adequate alternative explanation, reversible scavenging should be considered a necessary component in explaining the Nd paradox.

1. Introduction

1.1. The neodymium isotopic composition as a tracer for water-mass mixing

Different water masses in the ocean are characterised by distinct Nd isotopic compositions, the values of which are ultimately derived from the continents and delivered to the ocean through weathering, erosion, and particle–seawater interaction (Piepgras et al., 1979; Goldstein and O'Nions, 1981; Frank, 2002; Tachikawa et al., 2003; Goldstein and Hemming, 2003; Lacan and Jeandel, 2005). ^{143}Nd is produced by radioactive decay of ^{147}Sm, and ^{143}Nd/^{144}Nd in seawater is primarily a function of the age and lithology of the continental sources. Because this ratio only varies in the third or fourth digit, it is usually expressed as $\varepsilon_{\mathrm{Nd}}$, the parts per 10,000 deviation of a measured ^{143}Nd/^{144}Nd ratio from the “bulk Earth” value of 0.512638 (Jacobsen and Wasserburg, 1980).

In the global oceans two principal end members for dissolved Nd isotopic compositions are recognized. North Atlantic Deep Water (NADW) ($\varepsilon_{\mathrm{Nd}}=-13.5\pm0.5$; Piepgras and Wasserburg, 1987) has low values reflecting the old continental crust surrounding the North Atlantic. Deep water in the North Pacific has higher values ($\varepsilon_{\mathrm{Nd}}=-2$ to -4; for recent summaries see van de Flierdt et al., 2004 and Goldstein and Hemming, 2003) reflecting contributions from young volcanic arcs. Intermediate Nd isotopic compositions are found in Circum-Antarctic and Indian Ocean deep waters (Piepgras and Wasserburg, 1980, 1982; Bertram and Elderfield, 1993). Because Nd has an ocean residence time of ~200–2000 yr (Goldstein and O'Nions, 1981; Piepgras and Wasserburg 1983; Jeandel, 1993; Tachikawa et al., 1999; Tachikawa et al., 2003), long enough to be transported within the global thermohaline circulation system and short enough to avoid complete homogenisation, Nd isotope ratios in seawater have been used to trace water masses in the present and past ocean.

The potential use of Nd isotopes as a water-mass tracer is supported by a compilation of Nd isotope seawater measurements from the Atlantic Ocean, which appear to trace the distribution of water masses in the basin (i.e. NADW; Antarctic Intermediate Water, AAIW, and; Antarctic Bottom Water, AABW) (von Blanckenburg, 1999). The co-variation of Nd isotopes with water-mass tracers such as salinity is corroborated on a global scale (Goldstein and Hemming, 2003). These findings serve as the basis for the view that Nd isotopes can serve as a “quasi-conservative water-mass tracer” (see recent summaries in Frank, 2002; Goldstein and Hemming, 2003).

Recently, Piotrowski et al. (2005) reconstructed the first high-resolution record of Nd isotopes in the authigenic fraction of marine

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sediments from the Cape Basin (SE Atlantic) for the last glacial cycle, with the goal to reconstruct the strength of the Atlantic meridional overturning circulation over this interval. The record was produced by the preferential dispersal of Nd from the ferro-manganese oxide fraction of bulk sediments by sequential leaching of discrete samples from cores RC11-83 and TN057-21. The authors suggest that the variations in the record correlate with Greenland paleo-temperature, indicating that the fraction of NADW-derived Nd reaching the Southern Ocean increased during warm northern hemisphere interglacial and interstadial intervals and was reduced during glacials and stadial intervals (Rutberg et al., 2000; Piotrowski et al., 2004, 2005). Arsouze et al. (2008) suggested that these variations could be explained by changes to the $\varepsilon_{\mathrm{Nd}}$ value of NADW instead of changes to NADW intensity but this seems incompatible with the results of van de Flierdt et al. (2006) who found that the $\varepsilon_{\mathrm{Nd}}$ value of NADW was stable over the last glacial period.

There is obvious potential of Nd isotopes as a tool for understanding past changes in ocean circulation. However, any application of Nd isotopes as a circulation tracer, whether in the present or the past ocean, suffers from considerable gaps in existing knowledge about sources, sinks and internal cycling of Nd in seawater. Here we aim to address some of these issues by testing the importance of reversible scavenging for the marine Nd cycle in an ocean general circulation model for the first time.

1.2. Sources of neodymium to the ocean and the “neodymium paradox”

Although it is established that the continents are the major source of Nd to the ocean, the transport pathways of neodymium and how water masses acquire their neodymium isotopic composition are still unresolved (e.g., Frank, 2002; Goldstein and Hemming, 2003; van de Flierdt et al., 2004; Lacan and Jeandel, 2005). It has been shown that hydrothermal sources do not contribute to the dissolved seawater Nd budget in any significant way due to immediate removal of hydrothermal Nd at the vent site (e.g., Goldstein and O'Nions, 1981; Piepgras and Wasserburg, 1985; German et al., 1990; Halliday et al., 1992) but there is an ongoing debate on the relative importance of riverine versus aeolian sources of Nd to the ocean. The magnitudes of both fluxes are associated with considerable uncertainties due to removal (and remobilization) of Nd in estuaries on the one hand, and unknown dissolution rates of Nd from dust on the other hand (see Frank, 2002; van de Flierdt et al., 2004 for recent summaries). Applying literature estimates of global riverine and atmospheric fluxes from the 1990s, however, leads to a calculated residence time of Nd in the ocean on the order of 5000 yr (Bertram and Elderfield, 1993). This is not considered realistic because pronounced Nd isotopic differences are observed between water masses and large inter-basin gradients exist (e.g., Piepgras et al., 1979; Goldstein and O'Nions, 1981). These inter-basin gradients provide strong evidence for a residence time for Nd on the order of, or shorter than, the global turnover time of the ocean (1000 to 1500 yr; Broecker and Peng, 1982). These calculations indicate a missing source of Nd to the ocean, leading some authors to term this mass balance problem the “Nd paradox” (e.g., Bertram and Elderfield, 1993; Jeandel et al., 1995; see also van de Flierdt et al., 2004). Here we address, instead, the alternative definition of Goldstein and Hemming (2003), who state it as “the decoupling of Nd concentrations and isotopic compositions in the ocean”. Concentrations of Nd and other Rare Earth Elements in all the major ocean basins are relatively depleted in surface waters and enriched in deep waters, and there is an overall increase in concentrations from the North Atlantic to the North Pacific. With respect to these characteristics the concentrations of REEs follow a broadly similar distribution to silicate or phosphate in the ocean (e.g., Elderfield, 1988), and clearly are not conservative by the classical chemical oceanography definition. Neodymium isotopic compositions on the other hand are very distinct between the different ocean basins, and they show a pronounced structure in the water column which closely follows the distribution of deep-ocean water masses, giving Nd isotopes a ‘quasi-conservative’ character. For the purpose of this work, we will refer to the Nd paradox as the general mismatch between Nd isotopes, which tag water masses, and Nd concentrations, which reflect the internal cycling of Nd in the ocean.

No matter how we define the Nd paradox, whether in terms of mass balance, or in terms of a decoupling of concentrations and isotopes, the observational data clearly point to additional sources, sinks, and/or processes that play an important role in the oceanic Nd cycle. The observed distribution of Nd isotopes in seawater from the North Pacific is an interesting case in point. The high Nd isotope ratios found in this part of the ocean ($\varepsilon_{\mathrm{Nd}}=-2$ to -6; Piepgras and Wasserburg, 1980; Piepgras and Jacobsen, 1988; Shimizu et al., 1994; Amakawa et al., 2000, 2004; Vance et al., 2004) can be explained neither by input from large rivers nor from dust, as both of these sources exhibit more negative $\varepsilon_{\mathrm{Nd}}$ values than those associated with dissolved Nd in the North Pacific (see van de Flierdt et al., 2004 for a detailed discussion). To achieve an isotopic mass balance, local volcanic arcs must be a major source of Nd in the North Pacific, although, the mechanisms by which the Nd is added to the ocean remains unclear. For example, the input may involve interaction of river particulates with seawater, input of volcanic ash, and near bottom dissolution of deposited or resuspended sediments at the continent/ocean interface (e.g., Albarède and Goldstein, 1992; Elderfield and Sholkovitz, 1987; Spivack and Wasserburg, 1988; Bertram and Elderfield, 1993; Jeandel et al., 1995, 1998; Sholkovitz et al., 1999; Amakawa et al., 2000, 2004; Sholkovitz and Szymczak, 2000; Lacan and Jeandel, 2001, 2005). The importance of direct input via the flux of volcanic ash into the ocean may be amplified by the fact that volcanic ash is much more readily dissolved than continental material (e.g., Taylor and McLennan, 1985). Recently it has been suggested that submarine groundwater discharge may be a mechanism for introducing arc-like Nd to the ocean (Johannesson and Burdige, 2007).

Taking supply of Nd from the boundaries into account, Tachikawa et al. (2003) could calculate a residence time of 500 yr for Nd from box-model simulations of Nd concentrations in the global ocean. However, it has also been noted that water masses may interact with ocean margins to change their $\varepsilon_{\mathrm{Nd}}$ signature without additional input of Nd from the margin (Lacan and Jeandel, 2005). Lacan and Jeandel (2005) suggested the term “boundary exchange” to explain the alteration of isotope ratios at the ocean margins that cannot be accounted for by additional Nd input while acknowledging that the direct mechanism of this exchange reaction is not yet understood.

Here we will not address the detailed issues of Nd input to the ocean. Instead we focus on the internal cycling of Nd in the ocean. Our working hypothesis is that the quasi-conservative behaviour of Nd isotopes in deep waters along with increasing neodymium concentrations as water ages may be explained by a combination of lateral advection and vertical cycling via reversible scavenging. Here we will test this hypothesis for the fist time.

2. Method

2.1. Reversible scavenging

In an attempt to resolve the Nd paradox, we have applied the reversible-scavenging model of Bacon and Anderson (1982) to Nd isotope concentrations. Reversible scavenging is the process of isotope adsorption onto particles with subsequent desorption due to the release of the isotope during dissolution, particle aggregation/disaggregation, or variation in the dissolved isotope concentration. Note that the process of reversible scavenging relies on the physical process of particle adsorption/desorption onto particles and should not be confused with biological incorporation of REE. The use of a reversible-scavenging model for investigating the internal cycling of