Temporal stability of the neodymium isotope signature of the Holocene to glacial North Atlantic

Tina van de Flierdt,1 Laura F. Robinson,2 Jess F. Adkins,3 Sidney R. Hemming,1 and Steven L. Goldstein1

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[1] The neodymium isotopic composition of marine precipitates is increasingly recognized as a powerful tool for identifying changes in ocean circulation and mixing on million year to millennial timescales. Unlike nutrient proxies such as δ13C or Cd/Ca, Nd isotopes are not thought to be altered in any significant way by biological processes, and thus they can serve as a quasi-conservative water mass tracer. However, the application of Nd isotopes in understanding the role of thermohaline circulation in rapid climate change is currently hindered by the lack of direct constraints on the signature of the North Atlantic end-member through time. Here we present the first results of Nd isotopes measured in U-Th-dated deep-sea corals from the New England seamounts in the northwest Atlantic Ocean. Our data are consistent with the conclusion that the Nd isotopic composition of North Atlantic deep and intermediate water has remained nearly constant through the last glacial cycle. The results address long-standing concerns that there may have been significant changes in the Nd isotopic composition of the North Atlantic end-member during this interval and substantiate the applicability of this novel tracer on millennial timescales for paleoceanography research.


1. Introduction

[2] The water masses of the ocean display distinct Nd isotopic values that are ultimately derived from the continents and are delivered to the ocean through weathering, erosion, and particle-seawater interaction [Piepgras et al., 1979; Goldstein and O’Nions, 1981; Frank, 2002; Goldstein and Hemming, 2003; Lacan and Jeandel, 2005b]. The 143Nd is produced by radioactive decay of 147Sm, and the 143Nd/144Nd (expressed as εNd, which is the fractional deviation from the “bulk Earth” value of 0.512638 in parts per 10⁶ [Jacobsen and Wasserburg, 1980]) in seawater is primarily a function of the age of the continental source rocks. In the global oceans the two main end-members for dissolved Nd are North Atlantic Deep Water (NADW) (εNd = −13.5 ± 0.5 [Piepgras and Wasserburg, 1987]), with low values reflecting the old continental crust surrounding the North Atlantic, and deep water in the North Pacific (εNd = −2 to −3; for a recent summary see van de Flierdt et al. [2004]), with higher values reflecting contributions from circum-Pacific volcanics. The covariance of Nd isotopes with both salinity and dissolved silicate in Atlantic waters provide key evidence for the validity of Nd isotopes as a water mass tracer in the modern ocean [von Blanckenburg, 1999; Goldstein and Hemming, 2003]. Because Nd isotopes are not known to be affected by biological activity, or physical processes such as temperature and salinity, they can be used to assess ocean circulation changes that are independent of nutrient and carbon cycling [Frank, 2002; Goldstein and Hemming, 2003; Vance et al., 2004; Martin and Scher, 2004].

[3] Recently, Piotrowski et al. [2004, 2005] produced the first high-resolution seawater Nd isotope record over the last ~100 thousand years, based on Nd leached from the dispersed ferromanganese fraction of sediments from the Cape Basin in the South Atlantic. They interpreted the record to indicate greater NADW export during warm intervals on glacial-interglacial to millennial scales, including major interstadial events in the Greenland ice record. Focusing on the deglaciation, Piotrowski et al. [2004] concluded the “baseline” level of NADW export strength gradually intensified over the period between ~18 and 9 thousand years ago before present (kyr B.P.), with superimposed millennial variability.

[4] However, deglacial changes in the Nd isotopic composition of northern component waters could strongly affect this interpretation. Their assumption that it has remained nearly constant is based on data from surfaces of slow growing North Atlantic ferromanganese crusts and nodules, which generally show Nd isotope ratios similar to present-day NADW [Rutberg et al., 2000]. Short-timescale changes can be hidden because each crust and nodule sample represents an average of several glacial cycles.
There are distinct mechanisms through which the Nd isotopic signature of northern component waters may be altered on millennial to orbital timescales. First, the dominant fraction of modern NADW is formed by convection in the Labrador and Nordic Seas, where NADW source waters display a large range of Nd isotopic compositions (εNd of Labrador Seawater: −13.9 ± 0.4; Denmark Strait Overflow Water: −8.2 ± 0.6; Iceland-Scotland Overflow Water: −8.4 ± 1.4 [Lacan and Jeandel, 2004a, 2004b, 2005a]; Figure 1). A change in either the rate or place of formation of these key water masses could have a pronounced effect on the Nd isotopic composition of northern component waters. Secondly, changes in the style of weathering, the provenance of material, or the flux of material from the continents may significantly impact seawater Nd isotopic compositions [e.g., Burton et al., 1999; von Blanckenburg and O’Nions, 1999; Vance and Burton, 1999; Reynolds et al., 2004]. For example, a shift in continental weathering conditions (e.g., physical versus chemical) may cause incongruent release of Nd from different minerals leading to changes in the Nd isotopic composition of northern component source waters on short timescales [Öhlander et al., 2000; Andersson et al., 2001; von Blanckenburg and Nägler, 2001].

In order to address the question of possible North Atlantic end-member changes we use deep-sea corals to constrain the Nd isotopic composition of paleo-North Atlantic deep and intermediate waters. Our data indicate that there were no major changes in the Nd isotopic composition of the North Atlantic end-member over the last glacial cycle.

2. Samples, Methods, and Results

We investigated 10 solitary corals (eight Desmophyllum dianthus and two Caryophyllia), collected from the New England Seamounts from water depths between 1100 and 2500 m below sea level (mbsl) (Figure 2). Corals settle and grow on hard substrates, mainly in areas of swift ocean currents and low sedimentation, and fossil samples exposed to seawater typically acquire a black coating of ferromanganese oxides and oxyhydroxides (“crusts”). In order to remove this coating, each coral was subjected to a rigorous physical and chemical cleaning. Cleaned samples of 230–830 mg of carbonate were dissolved, passed through ion exchange chemistry, and precisely dated by U-Th disequilibrium by MC-ICP-MS [Edwards et al., 1986; Cheng et al., 2000; Robinson et al., 2002, 2005]. Mature North Atlantic Deep Water (NADW) carries a signature of −13.5 ± 0.5 [Piepgras and Wasserburg, 1987].
climate records to be generated from an individual coral. All corals of this study recorded a marine initial $\delta^{234}$U, indicating that they are free of diagenetic effects, and U series ages range from $\sim$0.3 to $\sim$90 ka (Table S1 in auxiliary material). We make the assumption that our cleaning procedure, designed to remove Th associated with ferromanganese coating, will also remove Nd, so that the remaining rare earth element (REE) abundances and Nd isotopic compositions reflect ambient seawater. Neodymium was extracted from the same sample as used for U-Th analyses (Table S2 in auxiliary material) and details on the method can be found in Table S2. Measurements were carried out on a VG Sector 54–30 thermal ionization mass spectrometer at Lamont.

Modern calibration of a 315 year old coral from the Gregg Seamount ($39^\circ 0' N$, $61^\circ 0' W$; 1176 mbsl) yielded $\varepsilon_{\text{Nd}} = -14.8 \pm 0.4$, within error of the modern value of $\varepsilon_{\text{Nd}} = -14.0 \pm 0.4$ of nearby seawater ($36^\circ 15' 38'' N$, $61^\circ 58' 27'' W$, 1100 mbsl [Piepgras and Wasserburg, 1987]). Further studies are required to show that deep-sea corals capture the full range of modern seawater Nd isotopic compositions, but preliminary data on $D. \text{dianthus}$ corals from the Drake Passage and the southwest Pacific indicate that deep-sea corals reflect the true Nd isotopic composition of surrounding seawater (T. van de Flierdt et al., unpublished data, 2006). The observation that REE are incorporated into the aragonitic lattice of shallow water corals approximately in proportion to their seawater concentrations [Sholkovitz and Shen, 1995] lends further support to the integrity of the marine Nd isotope signal in aragonitic coral skeletons.

The Nd isotope data for nine fossil corals from intermediate and deep waters over the past 91 kyr span a range of $\varepsilon_{\text{Nd}} = -12.1$ to $-14.8$, while those from only the intermediate depths show a narrower range of $\varepsilon_{\text{Nd}} = -13.4$ to $-14.8$ (Figure 2). Seven of the measured samples are from the deglacial interval, and the Younger Dryas (YD) time interval is especially well represented with five deep-sea coral ages from 11.6 to 12.6 kyr cal. B.P. (Figures 2b and 2c). Two more deglacial samples are from the time interval immediately following the Heinrich 1 event (H1) but preceding the Bolling warming (15.4 and 16.2 kyr cal. B.P.) (Figure 2b). The remaining two fossil samples are from marine isotope stages (MIS) 3 and 5, respectively (Figure 2a).

3. Discussion

Overall the deep-sea coral results indicate that there were no major changes in the Nd isotopic composition of the North Atlantic end-member over the last glacial cycle. As most of our samples are of deglacial age, we will focus our discussion on these samples.

3.1. Deglacial Nd Isotopic Composition in the Northwest Atlantic

The recently published Nd isotope record from the Cape Basin [Piotrowski et al., 2004] shows large deglacial

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variability (~4 $\varepsilon$ units), covering the entire amplitude of changes observed on glacial to interglacial timescales [Piotrowski et al., 2005]. Cape Basin Nd isotopic composition during the Younger Dryas and the time following H1 were higher (by 2–3 $\varepsilon$ units) than Holocene seawater, indicating a lower contribution of northern component waters as compared to today. Therefore the deglacial in the North Atlantic is a good period in which to evaluate whether the northern component end-member changed on glacial-interglacial timescales.

[12] Neodymium isotopes of deglacial deep-sea coral samples at intermediate water depth span a range of only 1.2 $\varepsilon$ units during the Younger Dryas, and the average value of $-14.3$, as well as each individual datum point, is consistent with the modern local seawater value of $\varepsilon_{Nd} = -14.0 \pm 0.4$ (Figures 2 and 3). Although the dominant water mass in the modern northwest Atlantic is NADW, during the YD the northwest Atlantic water column was similar to the Last Glacial Maximum (LGM), where modern NADW shoaled and transformed to its glacial analogue, Glacial North Atlantic Intermediate Water (GNAIW) [Boyle and Keigwin, 1987; Curry et al., 1988; Duplessy et al., 1988; Oppo and Lehman, 1993; Keigwin and Lehman, 1994; Sarnthein et al., 1994; Marchitto et al., 1998; Keigwin, 2004; Curry and Oppo, 2005]. GNAIW was most likely formed by convection south of Iceland [Duplessy et al., 1988; Oppo and Lehman, 1993; Sarnthein et al., 1994], and therefore south of the present-day convection in the Nordic Seas, and is thought to have filled the glacial North Atlantic down to depths of ~2000 m. Deeper waters in the glacial North Atlantic were derived from the Southern Hemisphere [Boyle and Keigwin, 1987; Curry et al., 1988; Duplessy et al., 1988; Marchitto et al., 2002; Keigwin, 2004; Curry and Oppo, 2005], and probably had higher Nd isotopic compositions. Our results show that GNAIW during the YD had the same Nd isotopic composition as modern NADW. Because of our limited data set we cannot exclude the possibility of Nd isotope changes of the North Atlantic end-member at other times during the deglaciation, but we consider such changes unlikely as our samples are from times of abrupt climate change (e.g., the Younger Dryas).

Our results confirm the value of Nd isotopes as a water mass and circulation tracer through time because they eliminate the long-standing concern that the Nd isotopic composition of the North Atlantic end-member has undergone substantial variability.

3.2. Acquisition of the NADW and GNAIW Nd Isotope Signal

[13] The results also have important implications for the manner in which GNAIW and NADW acquire their Nd isotopic compositions. In the present day, proto-NADW is formed downstream of the formation regions of Labrador Seawater (LSW), Iceland-Scotland Overflow Water, and Denmark Strait Overflow Water, through mixing in the subpolar gyre (Figure 1). LSW ($\varepsilon_{Nd} = -13.9$), Northeast Atlantic Deep Water (NEADW: $\varepsilon_{Nd} = -11.3$), and Northwest Atlantic Bottom Water (NWABW: $\varepsilon_{Nd} = -10.9$) are the direct precursors of NADW [Schmitz, 1996; Lacan and Jeandel, 2005a] and simple ternary mixing of these three water masses results in a predicted Nd isotope ratio of $\varepsilon_{Nd} = -11.7$ (calculation details are in auxiliary material). This value is outside of error of the mature NADW signature of $\varepsilon_{Nd} = -13.5$ and boundary exchange of deep waters with low $\varepsilon_{Nd}$ shelf sediments from the Greenland slope and the Labrador Sea has been suggested as a mechanism to obtain the Nd isotopic composition of NADW [Innocent et al., 1997; Lacan and Jeandel, 2005a].

[14] The similarity of the Nd isotopic signature of present-day NADW and GNAIW, as inferred from intermediate water depth YD deep-sea corals, implies that either (1) locations and/or processes associated with the acquisition of the Nd isotopic signature of GNAIW and NADW have been constant during glacial and interglacial climate change...
regimes, or (2) competing shifts in processes and/or locations lead to the same net result. Because convection in the NE Atlantic likely shifted from the Nordic Seas to the open North Atlantic south of Iceland during the LGM [Duplessy et al., 1988; Oppo and Lehman, 1993; Sarnthein et al., 1994], and glacial sea ice cover probably prevented vigorous convection in the Labrador Sea [Hillaire-Marcel et al., 2001], it is unlikely that GNAIW formed at the same locations as NADW does today. One possible mechanism to explain the similar Nd isotopic compositions is that convection or exchange of seawater with sediments south of Iceland (high $\varepsilon_{\text{Nd}}$) and on the Greenland shelf (low $\varepsilon_{\text{Nd}}$) imprinted a Nd isotopic signature to GNAIW resembling the modern contributions from the Nordic and Labrador Seas, respectively.

### 3.3. Influence of Southern Ocean Water

[15] Constraints on the water mass distribution in the glacial and deglacial North Atlantic are derived from various tracer data on benthic foraminifera ($\delta^{13}$C, Cd/Ca, radiocarbon) and indicate a water mass boundary between GNAIW and Southern Ocean waters at around 2000 to 2500 mbsl [Boyle and Keigwin, 1987; Curry et al., 1988; Duplessy et al., 1988; Marchitto et al., 2002; Keigwin, 2004; Curry and Oppo, 2005; Robinson et al., 2005]. Neodymium isotope ratios of four deglacial deep-sea coral samples from $\sim$2500 mbsl water depth cover a range of 1.4 $\varepsilon$ units ($\varepsilon_{\text{Nd}} = -12.1$ to $-13.5$). These values are slightly higher (average $\varepsilon_{\text{Nd}} = -12.8$) than modern NADW ($\varepsilon_{\text{Nd}} = -13.5 \pm 0.5$ [Piepgrass and Wasserburg, 1987]) and GNAIW ($\varepsilon_{\text{Nd}} = -14.3$), pointing to a mixture of GNAIW with Southern Ocean–derived waters. However, before we can determine quantitative mixing proportions of GNAIW and southern component water masses in the deep North Atlantic, we need better constraints on the composition of the southern end-member on glacial-interglacial timescales.

### 4. Conclusions

[16] We analyzed 10 deep-sea corals from the New England seamounts in the northwest Atlantic ranging in age from modern to 91 kyr cal. B.P. for their Nd isotopic compositions. The results provide direct evidence that GNAIW in the western North Atlantic had the same Nd isotopic composition as modern NADW. This conclusion is based on deep-sea corals that grew during the Younger Dryas, and is also confirmed by one sample from MIS 3. Stability of the North Atlantic end-member composition on glacial-interglacial timescales considerably simplifies interpretation of Nd isotope variability through time in other locations as a tracer of water mass mixing and ocean circulation.

[17] Future analyses of deep-sea corals will put tighter constraints on the glacial-interglacial Nd isotopic composition of both the northern and the southern end-member, and on their mixing ratio in the deep Atlantic over time. Additionally, since deep-sea corals are faithful archives for the radiocarbon contents of the past ocean [Robinson et al., 2005] coupled radiocarbon and Nd isotope analyses on deep-sea corals may open a new avenue of research in rapid climate change by providing a proxy to derive water mass fingerprinting and rates of overturning from the same, absolutely dated archive.

### References


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J. F. Adkins, Division of Geological and Planetary Sciences, California Institute of Technology, MS 100-23, 1200 E. California Boulevard, Pasadena, CA 91125, USA.
S. L. Goldstein, S. R. Hemming, and T. van de Flierdt, Lamont-Doherty Earth Observatory, Columbia University, 61 Route 9W, Palisades, NY 10964, USA. (tina@ldeo.columbia.edu)
L. F. Robinson, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Clark 448, MS 25, Woods Hole, MA 02543, USA.