



Testing the extraction of past seawater Nd isotopic composition from North Atlantic deep sea sediments and foraminifera

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[1] Neodymium isotopes provide a paleoceanographic proxy for past deep water circulation and local weathering changes and have been measured on various authigenic marine sediment components, including fish teeth, ferromanganese oxides extracted by acid-reductive leaching, cleaned foraminifera, and foraminifera with Fe-Mn oxide coatings. Here we compare Nd isotopic measurements obtained from ferromanganese oxides leached from bulk sediments and planktonic foraminifera, as well as from oxidatively-reductively cleaned foraminiferal shells from sediment cores in the North Atlantic. Sedimentary volcanic ash contributes a significant fraction of the Nd when the ferro-manganese (Fe-Mn) oxide coatings are leached from bulk sediments. Reductive leachates of marine sediments from North Atlantic core tops near Iceland, or directly downstream from Iceland-Scotland Overflow Waters, record ϵ_{Nd} values that are significantly higher than seawater, indicating that volcanic material is easily leached by acid-reductive methods. The ϵ_{Nd} values from sites more distal to Iceland are similar to modern seawater values, showing little contamination from Iceland-derived volcanogenic material. In all comparisons, core top planktonic foraminifera ϵ_{Nd} values more closely approximate modern deep seawater than the bulk sediment reductive leached value suggesting that the foraminifera provide a route toward quantifying the Nd isotopic signature of deep North Atlantic water masses.

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1. Introduction

[2] Neodymium (Nd) is a lithophile rare earth element with average concentrations of 20 to 40 ppm in the continental crust [Taylor and McLennan, 1985]. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio varies in rocks due to the radiogenic decay of ^{147}Sm , with a long half-life of 106 Ga [Faure, 1986]. The negative ϵ_{Nd} (where $\epsilon_{Nd} = \{[(^{143}\text{Nd}/^{144}\text{Nd})_{\text{measured}}/0.512638] - 1\} \times 10000$, using the accepted CHUR value from Jacobsen and Wasserburg [1980]) of seawater shows that it is mainly derived from the weathering of the continental crust. North Atlantic Deep Water (NADW), Antarctic Bottom Water (AABW), and the deep Pacific Ocean have distinct modern neodymium isotopic (ϵ_{Nd}) values of ~ -13.5 , ~ -8.0 , and ~ -4.0 , respectively [Piepgras and Wasserburg, 1982, 1987; von Blanckenburg and Nögler, 2001; Frank, 2002]. The less radiogenic ϵ_{Nd} values in the North Atlantic reflect the drainage of old cratonic material whereas the higher Pacific ϵ_{Nd} values reflect the dominance of inputs derived from arc magmatism. The ϵ_{Nd} of seawater is considered to be quasi-conservative within the oceanic water column and varies between water masses due to the short residence time Nd of 360 to 2,000 years [Frank, 2002; Arsouze et al., 2009]. Water mass mixing between these end-member water masses causes the ϵ_{Nd} of seawater to broadly covary with the salinity and nutrient content of deep waters, suggesting its use as a deep water source proxy.

[3] Early studies measured the Nd isotopic composition of ferromanganese nodules and crusts to reconstruct past seawater changes on long timescales of million years to tens of million years [O'Nions et al., 1978; Goldstein and O'Nions, 1981; Frank et al., 1999, 2002]. More recently, Nd isotopes have been measured on the dispersed Fe-Mn oxide coatings reductively leached from marine sediments, allowing for the observation of past changes in large-scale oceanic circulation patterns during glacial-interglacial cycles and millennial timescales [Rutberg et al., 2000; Bayon et al., 2002; Piotrowski, 2004; Piotrowski et al., 2005; Gutjahr et al., 2008; Pahnke et al., 2008]. Reasonable large-scale circulation reconstructions were also achieved by measuring the ϵ_{Nd} from other substrates, including; foraminifera with authigenic coatings [Palmer and Elderfield, 1985; Roberts et al., 2010], foraminifera cleaned of authigenic coatings [Scriver et al., 2004; Vance et al., 2004], fossil fish teeth or fish debris [Elderfield and Pagett, 1986; Martin and Haley, 2000; Scher and Martin, 2004; Via and Thomas, 2006; Roberts et al., 2010],

deep-sea corals [van de Flierdt et al., 2006; Robinson and van de Flierdt, 2009], and conodonts [Dopieralska, 2009]. However, ferro-manganese sediment coatings offer an opportunity to measure ϵ_{Nd} values on any deep-sea sediment at very high resolution, while the other substrates are not necessarily ubiquitous.

[4] Previous work using Nd isotopes from the Cape Basin [Rutberg et al., 2000; Piotrowski, 2004; Piotrowski et al., 2005, 2008], Angola Basin [Bayon et al., 2002], and North Atlantic Blake Ridge [Gutjahr et al., 2008] indicate large changes in the relative proportion of NADW and AABW on glacial-interglacial and millennial timescales. However, the three northern components of NADW also have distinct Nd isotopic signatures, with Iceland Scotland Overflow Water $\epsilon_{Nd} = \sim -8.4$, Denmark Straits Overflow Water $\epsilon_{Nd} = \sim -8.2$, and Labrador Sea Water $\epsilon_{Nd} = \sim -14.5$ [Piepgras and Wasserburg, 1987; Spivack and Wasserburg, 1988; Tachikawa et al., 1999; Lacan and Jeandel, 2004a, 2004b, 2004c; 2005a, 2005b; Godfrey et al., 2009; Rickli et al., 2009], and their relative proportions may have varied through time. The “unradiogenic” Labrador Sea Water indicates that ϵ_{Nd} of NADW is likely to be very sensitive to changes in this end-member, or that ϵ_{Nd} records from North Atlantic sites could trace past variability in NADW formation locations, which has been observed in other proxy records at various time scales [e.g., Duplessy et al., 1988; Hillaire-Marcel et al., 2001; Elmore and Wright, 2011]. A low-resolution record from deep-sea corals shows that the cumulative ϵ_{Nd} signature from the intermediate depth North Atlantic, representing the well-mixed NADW end-member, remained unchanged since the Last Glacial Maximum [van de Flierdt et al., 2006], whereas the data of Gutjahr et al. [2008] from Blake Ridge indicate a more radiogenic Nd isotopic composition of Glacial North Atlantic Deep Water.

[5] Despite the potential of ϵ_{Nd} to track high-frequency changes in deep water sourcing, little ground truthing of core top (near-modern) Fe-Mn oxide coatings and planktonic foraminiferal ϵ_{Nd} has been done, especially in the North Atlantic. Previous studies have noted the potential contribution of Nd from terrigenous sediments; Sr isotopes have been proposed to exclude this influence [e.g., Rutberg et al., 2000; Piotrowski, 2004; Piotrowski et al., 2005], however, Gutjahr et al. [2007] later showed that Sr isotopic evidence was insufficient for this task. The North Atlantic region provides a location to examine the utility of the Nd isotopic proxy in sediments with possible Nd influence from



both radiogenic (Iceland) and unradiogenic (North American and Canadian Cratons) sediments. Herein we present the ϵ_{Nd} measurements from Fe-Mn oxide coatings and foraminifera from core top locations throughout the North Atlantic, to evaluate the reliability of bulk sediment leachates as recorders of bottom water ϵ_{Nd} values.

2. Methods

[6] Site locations for the evaluation of core top measurements from Fe-Mn oxide leachates and foraminifera were chosen to cover a wide range of modern ϵ_{Nd} values, and to allow for the examination of individual sources to NADW (Table 1). The core top locations span a range of water depths from 400 to 4000 m, and are distributed throughout the northern North Atlantic, Norwegian Sea, and Labrador Sea, and over a variety of depositional settings including drift deposits, mid-ocean ridge, oceanic plateaus, and continental margins/slopes (Figure 1). The North Atlantic core tops are spatially distributed to capture the maximum and minimum ϵ_{Nd} values of North Atlantic bottom waters caused by varying proportions of the northern components of NADW, Iceland-Scotland Overflow Waters, Denmark Straits Overflow Water and Labrador Sea Water (LSW), which have distinct Nd isotopic values (Figure 1). From each core, samples were obtained from as close to the top of the core as possible and published chronologies have identified each of the ‘core top’ samples as recent (Table 1).

[7] The Fe-Mn oxide coating phase was extracted from decarbonated marine sediments by reductive leaching, according to the methods outlined in the work by *Rutberg* [2000], after *Chester and Hughes* [1967]. Carbonate was first removed from ~2 cc of dry bulk sediment by leaching with a buffered weak acetic acid. The remaining terrigenous fraction was rinsed two to three times with deionized water, and then leached with 0.02 M hydroxylamine hydrochloride for 1 h. The leachates were dried and converted to a nitric acid matrix before ion exchange column chromatography for separation and purification of Nd.

[8] Approximately 50 mg of planktonic foraminifera for neodymium isotopic analyses were picked from the >150 μm size fraction of washed samples [*Scriver et al.*, 2004; *Roberts et al.*, 2010]. The selected tests were crushed to break all chambers, and ultrasonicated in deionized water three times for 1 min each time, until the calcite was free of macroscopic clays. The calcite fragments were then examined under a microscope and any fragments

with detrital contamination were removed. The foraminiferal fragments from some samples were split, and one portion was oxidatively-reductively cleaned using a method outlined in the work by *Roberts et al.* [2009], modified from *Boyle* [1981]. Each oxidative-reductive subsample was cleaned with a reductive solution (1 part 1 M hydrous hydrazine; 6 parts 16 M NH_4OH ; 3 parts 0.25 citric acid and 16 M NH_4OH) in a hot water bath for 30 min at 80°C, while repeatedly sonicating for 10 s every 2.5 min. Samples were then cleaned with an oxidative solution (1 part 0.2 M NaOH; 1 part 30% H_2O_2) in a hot water bath for 30 min at 80°C, while repeatedly sonicating for 30 s every 10 min. Oxidative-reductive samples were then leached in weak acid (0.001 M HNO_3) while sonicating for 5 min, and then dissolved in dilute (less than 1 Molar) acetic acid. Subsamples that were not oxidatively-reductively cleaned are herein termed, ‘unclean,’ and were dissolved in dilute (less than 1 Molar acetic acid) following removal of detrital contamination.

[9] For ferromanganese oxides leachates and foraminiferal samples, rare earth elements (REE) and other cations were chemically isolated from the sample using volumetrically calibrated columns with Eichrom TRUspec© resin (TR-B25-A). The REE aliquot was then further separated to isolate the neodymium fraction using columns of Eichrom LNspec© resin.

[10] Neodymium isotopic compositions were measured on a Nu Plasma multiple-collector inductively coupled plasma mass spectrometer at the University of Cambridge [e.g., *Halliday et al.*, 1998]. An exponential-fractionation correction was employed to account for mass fractionation, by normalizing $^{146}\text{Nd}/^{144}\text{Nd}$ to 0.7219. Samples were bracketed by JNdi-1 standards and corrected to the published value of 0.512115 ± 7 [*Tanaka et al.*, 2000]. External errors were calculated from bracketed JNdi-1 measurements during the batch analysis. Errors for foraminiferal samples were larger due to the smaller amount of Nd being analyzed, caused by its low concentration in foraminiferal calcite [e.g., *Vance and Burton*, 1999; *Pomies et al.*, 2002; *Vance et al.*, 2004; *Martinez-Boti et al.*, 2009; N. L. Roberts et al., Rare earth element association with foraminifera, submitted to *Geochimica et Cosmochimica Acta*, 2011].

3. Results

3.1. Core Top Fe-Mn Oxide Leachate

[11] Core top Fe-Mn oxide leachate ϵ_{Nd} values in the North Atlantic range from +3.1 to -19.5 epsilon units (Figure 2 and Table 1). Deep and intermediate



Table 1 (Sample). Sample Number, Core Name, Core Depth, Reference for Chronology, Latitude, Longitude, and Water Depth and Bulk Sediment Leachate ϵ_{Nd} , Uncleaned Planktonic Foraminifera ϵ_{Nd} , and Oxidatively/Reductively Cleaned Planktonic Foraminifera ϵ_{Nd} ^a [The full Table 1 is available in the HTML version of this article]

Site	Core	Core Depth (cm)	Reference for Chronology	Lat.	Long.	Water Depth (m)
1	VM30-163	0-1	http://www.esc.cam.ac.uk/delphi/coredata/wwwcoredata/VEMA/v30_163.html	72.4	14.8	748
2	VM28-16	0-1	-	67.1	-25.6	955
3	KN177-2 MC35	2-3	Elmore [2009]	65.4	-4.7	3924
4	KN177-2 GGCI7	1-2	Scrivner et al. [2009]	62.8	1.3	965
5	KN177-2 MC4	2-3	Elmore [2009]	62.1	2.7	418
6	Rapid12-1K	8-9	Thornalley et al. [2009]	62.1	-17.8	1938
7	Rapid17-5P	8-9	Thornalley et al. [2009]	61.5	-19.5	2303
8	KN166-14 2 JPC	0-2	-	61.0	-22.3	1880
9	HM03-133-25 (<150um)	2-3	Solignac et al. [2008]	60.1	-6.1	1160
10	BOFS17K	0-1	Maslin et al. [1995]	58.0	-16.5	1150
11	KN166-14 19 JPC	0-2	Neizke [2006]	57.5	-47.6	2500
12	RAPID 21-12B	3.5-4	Iglesias-Rodriguez et al. [2008]	57.5	-27.9	2630
13	KN166-14 21 GGC	0-2	Henderson [2009]	57.2	-48.8	2800
14	KN166-14 10 GGC	0-2	Elmore [2009]	56.2	-27.4	2707
15	KN166-14 3 GGC	0-2	-	55.3	-26.3	3305
16	BOFS11K	11-12	Yu et al. [2008]	55.2	-20.3	2004
17	BOFS10K	2-3	Yu et al. [2008]	54.7	-20.7	2777
18	KN166-14 12 JPC	0-2	-	53.1	-33.5	3078
19	VM28-77	0-1	-	53.0	-16.8	2036
20	BOFS 5k	33-34	Yu et al. [2008]	50.6	-21.9	3547
21	VM27-17	0-2	Ruddiman [1992]	50.1	-37.3	4054
22	VM23-16	0-2	Bond et al. [1993]	45.1	-46.0	2813
23	CHN82-23	28-29	Sosdian [2008] and Sosdian and Rosenthal [2009]	43.0	-31.0	3406
24	306 UI313	15-17	Voelker et al. [2010]	41.0	-33.0	3426
25	VM28-89	6.25	Piotrowski [2004]	44.5	-32.6	3640
26	VM26-17	0.5	Piotrowski [2004]	29.9	-45.1	3620
27	VM20-96	5	Piotrowski [2004]	40	-33.1	3190
28	OCE236-GGC6	4-5	Roberts et al. [2010]	33.7	-57.6	4541
29	ODP172-1063	2-4	Roberts et al. [2010]	33.7	-57.6	4541
30	KNR140 51GGC	40	Guñajahr et al. [2008]	32.0	-76.0	1790
31	KNR140 12JPC	20	Guñajahr et al. [2008]	29.0	-73.0	4250
32	ODP172-1061	13-15	Roberts et al. [2010]	29.0	-73.0	4250
33	KNR140 31GGC	Coretop	Guñajahr et al. [2008]	30.9	-74.5	3410
34	BOFS 8k	1-2	Yu et al. [2008]	52.5	-22.1	4045

^aThe closest available water column data is also given. Data from this study are in bold. Lat., latitude; Long., longitude.

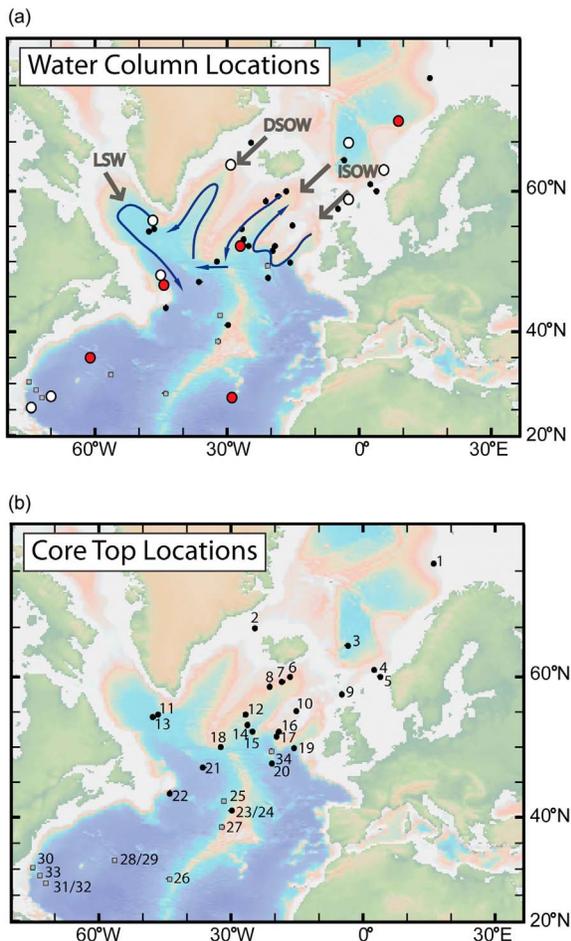


Figure 1. (a) Map of the North Atlantic showing the three northern sources of deep water, Iceland-Scotland Overflow Water (ISOW), Denmark Straits Overflow Water (DSOW), and Labrador Sea Water (LSW), and generalized current paths. Solid black circles show sites with core top neodymium isotopic measurements from this study; previously published studies are also shown (gray squares). Locations of water column measurements are shown as larger circles; red circles represent the locations of water column measurements displayed in Figure 4, white circles represent locations of all water column measurements displayed in Figures 5 and 6. (b) Map of the North Atlantic showing the numbered core top locations used in this study.

seawater ϵ_{Nd} values for the North Atlantic region vary between ~ -8 and -15 , with much of the variation corresponding to individual water masses [Goldstein and Hemming, 2003, and references therein]. Sixteen of the 34 core top Fe-Mn oxide leachates fell within the limits of modern seawater values (Table 1), with most reductively leached samples in the midlatitude North Atlantic, south of

$\sim 50^\circ\text{N}$, have core top leachate ϵ_{Nd} values similar to modern local seawater values, ranging from -7.9 to -13.2 (Figure 2), reflecting the heterogeneity of the different components of NADW (Greenland/Norwegian Seas = ~ -8.3 and Labrador Sea = ~ -14.5 [Lacan and Jeandel, 2005a, 2005b]).

[12] Core top locations proximal to Iceland and along the paths of Norwegian Sea overflows, including the Bjorn and Gardar Drifts, have particularly high core top leachate Nd isotopic values (-2.6 to $+3.1$), which are outside of the range of modern seawater values so far observed (Figure 2 and Table 1). Since the ϵ_{Nd} value of Icelandic-derived material is $+5$ to $+10$ [Cohen and O’Nions, 1982; Hemming, 2004], the elevated ϵ_{Nd} values are most likely caused by contamination by local volcanogenic Icelandic-derived material, either during leaching in the laboratory or in situ, during formation of Fe-Mn oxides. The more distal Eirik Drift, south of Greenland, also recorded elevated ϵ_{Nd} values (-2.6 to -4.8), which indicates substantial downstream transport of Icelandic-derived sediments via Denmark Straits Overflow Water [Worthington, 1976; Kissell et al., 2008] (Figures 1 and 2).

[13] Deviations from seawater Nd isotope values in core tops using reductive leachates are not restricted to the region proximal to Iceland (Figure 2). Site 27 (VM20-96), located near the Azores, has a leachate-derived ϵ_{Nd} value of -5.5 (Figure 2 and Table 1), which is higher than proximal seawater ϵ_{Nd} values (-6.26 at 50 m, -13.6 at 1004 m, and -9.66 at 5506 m [Godfrey et al., 2009]). The ϵ_{Nd} values of $+4.1$ to $+5.7$ are reported for volcanic material from the Azores Islands [Franca et al., 2006], and thus volcanogenic material is considered a likely contributor to the core top reductively leached neodymium at site 27 (VM20-96). Aeolian material in the Atlantic region has ϵ_{Nd} values from -14.2 to -10.5 ϵ_{Nd} [Grousset et al., 1988], and is therefore too negative to be the contaminant at site 27 (VM20-96). Other sites in this region have reductive leachate compositions similar to modern seawater ϵ_{Nd} compositions, arguing for a locally derived volcanogenic source of contamination.

[14] The core top reductive leachate from site 22 (VM23-16), east of Newfoundland and south of the Flemish Cap, recorded the lowest ϵ_{Nd} value of -19.5 , suggesting contamination by unradiogenic Nd from sediments derived from the Canadian Shield (Figure 2 and Table 1). However, Lacan and Jeandel [2004a, 2004b, 2004c] proposed that Nd isotopic values may reflect local modern seawater derived from the Labrador Sea or influenced by

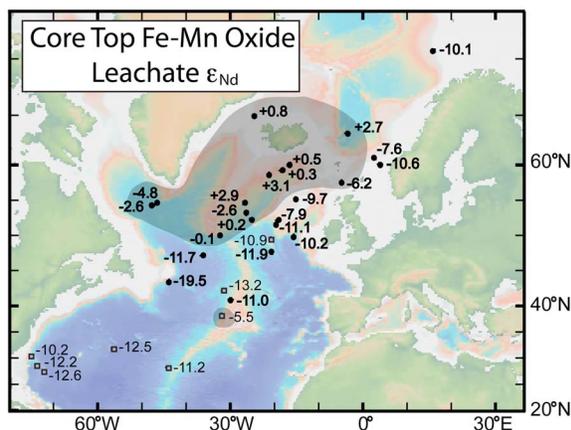


Figure 2. Map of North Atlantic core top bulk sediment Fe-Mn oxide leachate ϵ_{Nd} from this study (black circles, bold text values) and previous studies (gray squares, plain text values). The shaded regions denote areas where core top Fe-Mn oxide leachates are presumed contaminated by volcanogenic material transported from Iceland via bathymetric currents or from the Azores.

boundary exchange. The unradiogenic value could also indicate a contamination of the seawater signal by in situ pore water fluid interactions with remobilized glacial flour.

3.2. Core Top Uncleaned Planktonic Foraminifera

[15] Eight of the 12 North Atlantic core top uncleaned mixed species planktonic foraminiferal samples have ϵ_{Nd} values that fall within the range of modern North Atlantic bottom water (−10 to −14; Table 1 [Piegras and Wasserburg, 1987; Spivack and Wasserburg, 1988; Tachikawa et al., 1999; Lacan and Jeandel, 2004a, 2004b, 2005a, 2005b; Godfrey et al., 2009; Rickli et al., 2009]), particularly those from south of $\sim 50^\circ N$ (Figure 3a and Table 1). However, the not reductively cleaned, henceforth called “uncleaned” foraminifera from the location nearest to Iceland (site 8; KN166-14 2JPC) recorded an ϵ_{Nd} value of −2.3, which is far more radiogenic than proximal seawater [Lacan and Jeandel, 2004b]. Uncleaned planktonic foraminifera from Eirik Drift (site 11; KN166-14 19JPC) recorded an ϵ_{Nd} value of −8.6, which is also more radiogenic than proximal seawater [Lacan and Jeandel, 2004a]. This indicates that the contribution of Icelandic volcanogenic material contaminates uncleaned foraminifera both near Iceland and through transport by bathymetric currents. This contamination could occur through adherence of particulates, chemically during processing in the laboratory, or in the sediments while

the foraminifera are exposed to pore water fluids. Similarly, the location nearest to LSW outflow (site 22; VM23-16) recorded an unradiogenic ϵ_{Nd} value of −23.3, suggesting contamination from the unradiogenic Canadian Craton (Figure 3a and Table 1).

3.3. Core Top Oxidatively-Reductively Cleaned Planktonic Foraminifera

[16] Oxidatively-reductively cleaned mixed species planktonic foraminifera from core tops around the North Atlantic basin have ϵ_{Nd} values that range from −6.8 to −23.4, with 10 of the 13 ϵ_{Nd} values approximating modern surface or deep North Atlantic seawater (Figure 3b and Table 1). Both cleaned and uncleaned foraminifera are, therefore, closer to approximating seawater ϵ_{Nd} values than the Fe-Mn oxide leachates. As with the uncleaned planktonic foraminifera, core top foraminifera from Eirik Drift (11; KN166-14 19JPC and 13; KN166-14 21JPC) record ϵ_{Nd} values (−8.7 and −6.8, respectively) that are more radiogenic than seawater; since foraminifera are unlikely to be transported by bathymetric currents [e.g., Keigwin and Schlegel, 2002], radiogenic values indicate either transport of Icelandic material contaminating foraminiferal analyses or modification of the deep waters by Icelandic material owing to boundary exchange. Cleaned planktonic foraminifera from site 22 (VM23-16), south of the Flemish Cap, also record a more unradiogenic ϵ_{Nd} value (−23.4) suggesting Canadian Cratonic influence despite oxidative-reductive cleaning (Figure 3b).

4. Discussion

4.1. Core Top Fe-Mn Oxide Leachate

[17] Evaluation of North Atlantic core top Fe-Mn oxide sediment coating leachates indicates that Icelandic volcanogenic material is capable of contaminating leachate ϵ_{Nd} values (Figure 2). Cores in the vicinity of Iceland, and also within the path of overflow waters, have core top values significantly shifted from seawater composition toward that of Iceland basalt. Long distance sediment transport from Iceland is also suggested by this pattern, as core top leachates from the Eirik Drift, south of Greenland are significantly shifted toward Icelandic composition (e.g., site 11 KN166-14 19JPC ϵ_{Nd} −4.82; site 13 KN166-14 21GGC ϵ_{Nd} −2.58). This suggests that leaching sediment with even a small volcanic-derived component will yield ϵ_{Nd} values that are isotopically more positive than seawater (Figures 4–6 and Table 1).

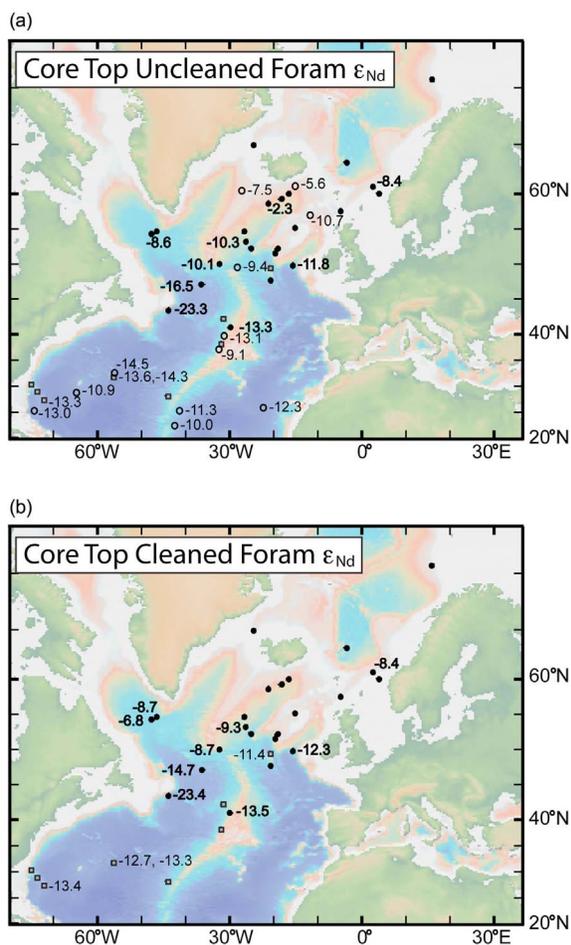


Figure 3. (a) Map of ϵ_{Nd} from uncleaned planktonic foraminifera (with authigenic coatings) from core tops from this study (black circles, bold text values) and previous studies (gray boxes, normal text values). Published data from *Palmer and Elderfield* [1985] are shown as distinct symbols (open circles, narrow text) to indicate that the samples were processed differently. (b) Map of core top ϵ_{Nd} from oxidatively-reductively cleaned planktonic foraminifera (without authigenic coatings) from this study (black circles, bold text); previously published values are indicated by gray boxes and normal text.

[18] In addition to the pervasive contribution of Icelandic volcanogenic material to Fe-Mn oxide leachate Nd, sites 27 (VM20-96) near the Azores and 22 (VM23-16), east of Newfoundland also have core top leachates that differ from modern North Atlantic seawater (Figures 2 and 4). This suggests that some sources of sediment derived from both volcanic islands and continents also complicate the measurement of Nd through the sediment leaching method. Clearly leachate records from cores located near, or along the transport path of, an input of volcanic or continental sediment to the intermediate and deep ocean must be treated with skepticism.

[19] Easily altered and easily leached volcanogenic silicate sediment is either affecting the neodymium isotopic signature during the acid-reductive leaching in the laboratory, possibly in situ within the sediments through boundary exchange [*Lacan and Jeandel, 2005a, 2005b*]. Methodological experiments have shown that sample size, reagent strength, and leaching time effect ϵ_{Nd} values suggesting a laboratory component to the contaminating phase [*Gutjahr et al., 2007; Wilson et al., 2009*]; however, we cannot rule out that the Fe-Mn oxide coating ϵ_{Nd} values have been altered by addition of Nd from volcanogenic sediment at the sediment-water interface [*Lacan and Jeandel, 2005a, 2005b*].

[20] In contrast, core top leachates from sites in the mid-North Atlantic that are distal from sediment inputs have a Nd isotopic composition that is within the range of modern North Atlantic intermediate and deep waters. This suggests that the pelagic sediments at these locations are less likely to release Nd during acid-reductive leaching in the laboratory, or in nature. It could also be suggested that the Nd isotopic composition of fine pelagic clays in the central mid-North Atlantic are isotopically indistinguishable from the leachable fraction, however the North Atlantic Nd isotope map of *Grousset et al.* [1988] shows that silicate fraction ϵ_{Nd} compositions of -12 to -14 are common in regions where we are leaching Nd isotopic compositions of -11 (Figure 2).

[21] Clearly, our core top calibration map of leachate Nd isotopic compositions shows a regional variability, suggesting that records from sites with any contribution of volcanogenic or easily altered sediments are suspect for paleoceanographic interpretation. Cores that are sufficiently distal to sediment inputs may be reliable for paleoreconstruction, although their sensitivity to past changes in silicate sediment sourcing must be understood. Of particular interest would be the possible contamination of the bottom water Nd isotopic signature by unradiogenic terrestrial carbonate transported from the Canadian Craton to the North Atlantic via ice rafting during Heinrich Events.

4.2. Core Top Planktonic Foraminifera

[22] Comparison of Figure 2 with Figures 3a and 3b show that both the uncleaned and oxidatively-reductively cleaned core top foraminifera record Nd isotopes that are closer to modern seawater values than the leachate method in nearly all locations (-10 to -14 [*Piepgras and Wasserburg, 1987; Spivack and Wasserburg, 1988; Tachikawa et al.,*

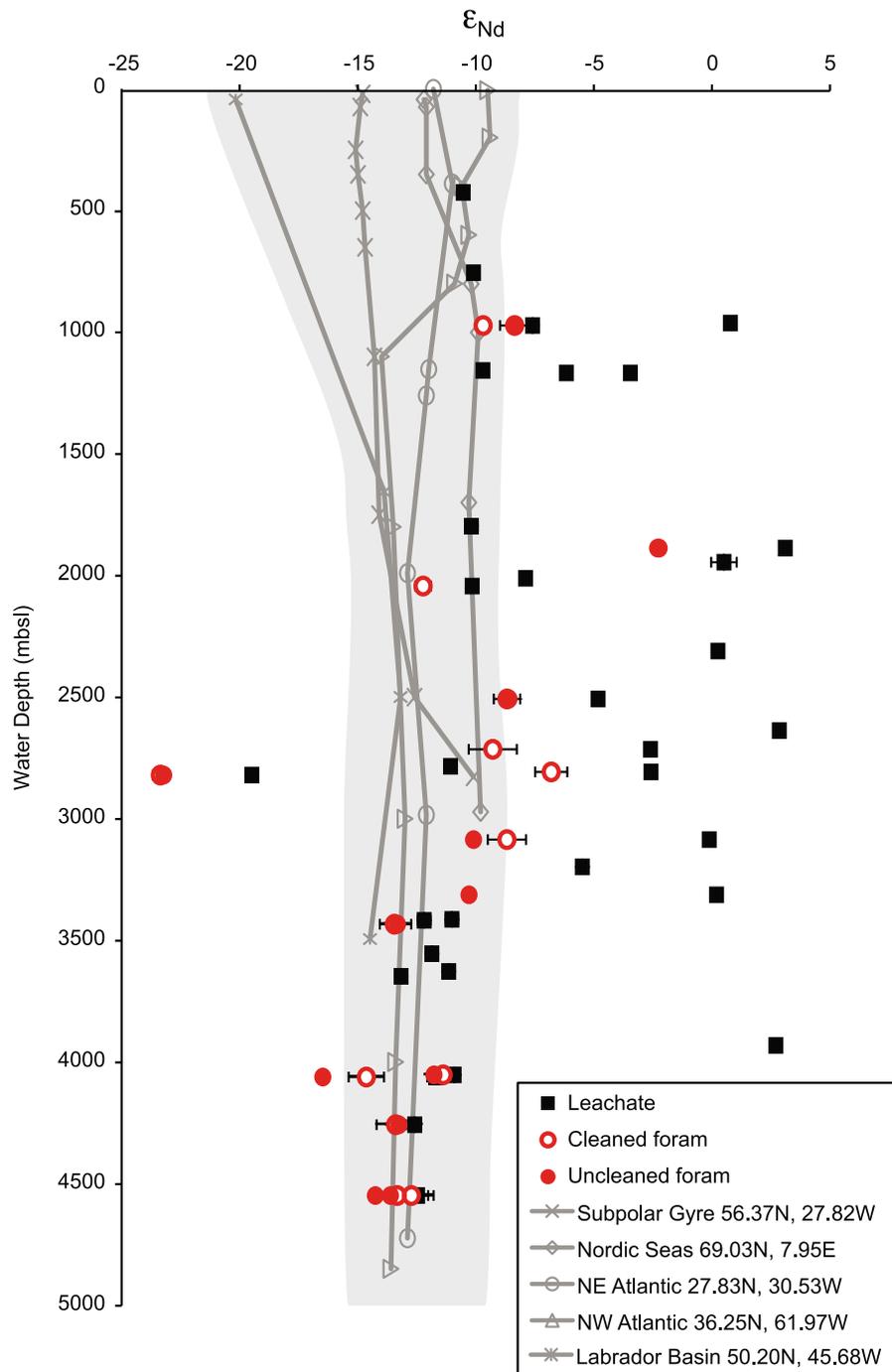


Figure 4. Leachate, oxidatively-reductively cleaned planktonic foraminifera, and uncleaned planktonic foraminifera (with authigenic coatings) ϵ_{Nd} values for all cores shown with water depth. Error bars are shown for all samples but are often smaller than the data symbol. Seawater ϵ_{Nd} profiles are also shown, sorted into geographic regions from Piepgras and Wasserburg [1983], Stordal and Wasserburg [1986], Piepgras and Wasserburg [1987], Spivack and

1999; Lacan and Jeandel, 2004a, 2004b, Lacan and Jeandel, 2005a, 2005b; Godfrey et al., 2009; Rickli et al., 2009]. In the immediate vicinity of Iceland (e.g., site 8; KN166-14 2JPC), both the Nd isotopic

composition of the core top sediment leachate (+3.12) and the uncleaned planktonic foraminiferal (-2.27) are offset from modern seawater values (-8 to -11 [Lacan and Jeandel, 2004b]); though



the foraminifera more closely approximate seawater values than the leachates (Figures 2, 3b, and 5b). However, cores further south of Iceland (e.g., site 18; KN166-14 12JPC) with core top leachate Nd isotopic compositions that are offset from modern

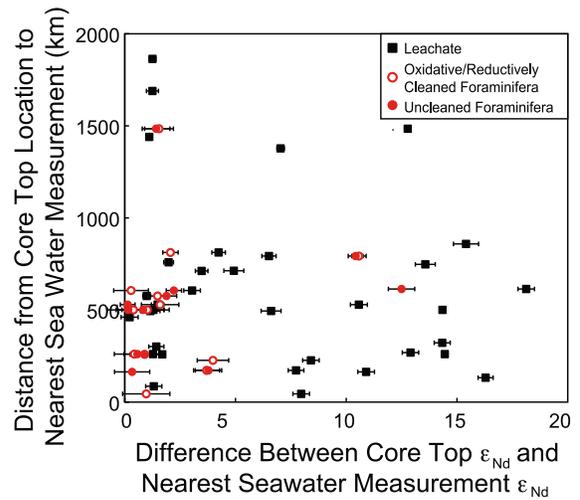
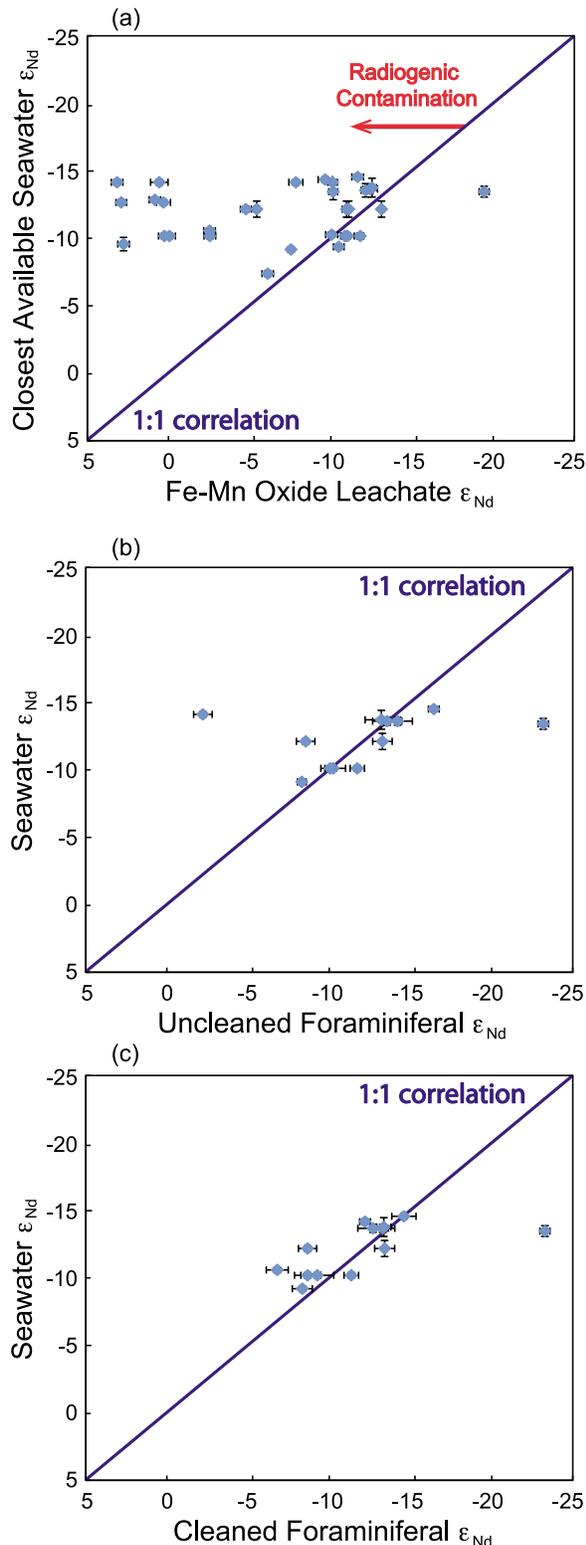


Figure 6. Crossplot of the difference between core top Fe-Mn oxide leachate ϵ_{Nd} (black squares), oxidatively-reductively cleaned planktonic foraminiferal ϵ_{Nd} (open red circles), and uncleaned planktonic foraminiferal ϵ_{Nd} (red circles; with authigenic coatings) and the nearest seawater ϵ_{Nd} measurement at a similar depth plotted against the distance between the core top site and the seawater measurement. No noticeable trend exists between the ϵ_{Nd} variance and distance between the locations, further demonstrating that the core top leachate ϵ_{Nd} samples are significantly offset from seawater. Data are available in Table 1.

seawater toward Icelandic basalts (-0.11) have uncleaned foraminiferal Nd isotopes (-10.11) and oxidatively-reductively cleaned planktonic foraminiferal Nd isotopes (-8.69) that approximate modern seawater (-8 to -11 [Lacan and Jeandel, 2004b]). This suggests that planktonic foraminifera are a more reliable archive of seawater Nd isotopes than Fe-Mn oxide sediment leachates, minimizing the effects of Icelandic derived volcanogenic material. A full quantitative assessment and discussion of where the Nd isotope signal is “locked in” the foraminifera, as well as diagenetic processes, pore water mobilization, and rescavenging is given in the work by Roberts et al. (submitted manuscript, 2011).

Figure 5. Crossplots of ϵ_{Nd} of seawater from an approximate depth at the closest available location to core top (a) Fe-Mn oxide leachate ϵ_{Nd} , (b) oxidatively-reductively cleaned planktonic foraminiferal ϵ_{Nd} , and (c) uncleaned planktonic foraminiferal ϵ_{Nd} (with authigenic coatings). Seawater locations are given in Table 1, and locations are shown on Figure 1. An idealized 1:1 correlation, indicating no difference between core top measurements and seawater is shown as a bold blue line. The red arrow on Figure 5a represents the direction of radiogenic ϵ_{Nd} contamination of the Fe-Mn oxide leachates.

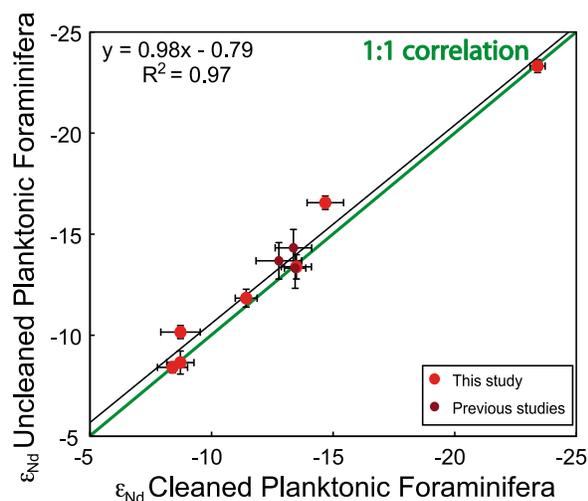


Figure 7. Crossplot of ϵ_{Nd} from uncleaned planktonic foraminifera and oxidatively-reductively cleaned planktonic foraminifera from this study (red circles); data from *Roberts et al.* [2010] are shown as purple circles and are included in the linear regression (black line). An idealized 1:1 correlation, indicating no difference between uncleaned and oxidatively-reductively cleaned planktonic foraminifera is shown as a bold green line.

[23] The improved relationship between foraminiferal Nd isotopes and seawater can also be seen when comparing variations of core top leachates, oxidatively-reductively cleaned planktonic foraminifera and uncleaned planktonic foraminifera, to depth variations in seawater Nd isotope profiles (Figures 4, 5b, 5c, and 6). Of the three sample types, the leachates are most different from seawater at all depths, usually shifted to radiogenic values (Figure 4). The planktonic foraminifera, both oxidatively-reductively cleaned, and those with authigenic coatings, largely match North Atlantic seawater profiles, especially at the deeper sites (>3000 m) and when located distally from continental margins. This suggests that foraminiferal coatings are a more reliable phase to extract past seawater Nd isotopes than leaching of bulk sediment.

[24] Most of our data from sites around the North Atlantic, suggest that there is no significant difference in Nd isotopes between oxidatively-reductively cleaned foraminifera and those which have authigenic coatings, that but have been cleaned of clay and silicate minerals (Figures 3a and 3b). In fact, there is a strong correlation between the uncleaned and cleaned foraminiferal ϵ_{Nd} values from the same (or very closely neighboring) sites, lying mostly within error of a 1:1 relationship (slope of 0.95, R^2 value 0.97; Figure 7). However, some samples of uncleaned planktonic foraminifera (e.g., site 21

VM27-17, site 18 KN166-14 12JPC, and site 28 OCE236-GGC6) have ϵ_{Nd} values that are up to 2 epsilon units more negative than their oxidatively-reductively cleaned counterparts (Figures 4 and 7).

[25] There are at least 2 explanations for uncleaned planktonic foraminifera to record more negative ϵ_{Nd} values than cleaned planktonic foraminifera; first, while the uncleaned foraminifera have had all visible clay and minerals removed, they may contain trace quantities of microscopic (or perhaps interstitial) clays or lithogenic material with unradiogenic Nd, which are subsequently removed during the oxidatively-reductively cleaning procedure. Second, uncleaned planktonic foraminifera have bottom water-derived authigenic Fe-Mn oxide coatings, while cleaned planktonic foraminifera record ϵ_{Nd} values that are relatively more surface water derived, which may be more isotopically positive in parts of the North Atlantic (Figure 4). This result may support previous studies that showed living planktonic foraminifera contained a significant quantity of surface water Nd at some locations [*Vance and Burton*, 1999; *Pomies et al.*, 2002; *Vance et al.*, 2004; *Martínez-Boti et al.*, 2009], which has been largely discounted (*Roberts et al.*, submitted manuscript, 2011). However, it is clear that the cleaned and authigenically coated fossil foraminifera record a bottom water signature at most intermediate and deep water North Atlantic sites (Figure 4), in agreement with *Roberts et al.* [2010], who showed that planktonic foraminifera that have not been oxidatively-reductively cleaned contain a deep water signature at the Bermuda Rise. Further, *Roberts et al.* (submitted manuscript, 2011) showed that the majority of the Nd in fossil planktonic foraminifera results from deep water processes of remineralization and scavenging.

[26] The fact that a few cleaned foraminifera from North Atlantic sites (e.g., site 13 KN166-14 21GGC; ϵ_{Nd} -6.81) do not match modern surface or deep water suggests that meticulous cleaning and removal of all silicate detritus may be important, or that some foraminiferal authigenic coatings were formed from pore waters precontaminated by Nd derived from locally derived sediment. It is worth noting that the reductively cleaned planktonic foraminiferal samples that do not match modern seawater are from locations where the leachates are strongly offset from the seawater compositions. This suggests that insufficient cleaning of silicate sediment from foraminiferal calcite could also play a role in causing a discrepancy between oxidatively-reductively cleaned and uncleaned foraminiferal Nd isotopes measurements. The idea that there may be



locations in the ocean, perhaps in oxygen poor environments where authigenic coatings cannot form, and where fossil planktonic foraminiferal Nd isotopes can more accurately record surface water is worth further investigation.

5. Conclusions

[27] Our new data from deep-sea sediment cores indicates that ϵ_{Nd} values from the acid-reductive leaching of bulk sediments can be contaminated by volcanogenic and possibly continentally derived silicate sediment that is derived proximally or transported by bathymetric currents. Marine sediment core records of Nd isotopes are especially susceptible to contamination from volcanically derived sediments and fine-grained glacial flour, which may be easily altered. Despite these contaminating phases, Fe-Mn oxide leachates that are distal to volcanic sources may be valuable recorders of seawater ϵ_{Nd} values.

[28] At most core top sites, both uncleaned and oxidatively-reductively cleaned planktonic foraminifera record ϵ_{Nd} values that are similar to regional deep seawater ϵ_{Nd} values. Therefore, future studies should focus on the measurement of foraminifera, which appear to more closely record modern deep water compositions, although careful cleaning of silicate detritus may be important, especially in areas proximal to easily leached (volcanogenic or cratonic) sediment inputs.

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