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Constraining erosional input and deep-water formation in the North Atlantic using Nd isotopes

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Abstract

Many marine radiogenic isotope records show both spatial and temporal variations, reflecting both the degree of mixing of distinct sources in the oceans and changes in the distribution of chemical weathering on the continents. However, changes in weathering and transport processes may themselves affect the composition of radiogenic isotopes released into seawater. The provenance of physically weathered material in the Labrador Sea, constrained through the use of Ar–Ar ages of individual detrital minerals, has been used to estimate the relative contributions of chemically weathered terranes releasing radiogenic isotopes into the Labrador Sea. A simple box-model approach for balancing observed Nd-isotope variations has been used to constrain the relative importance of localised input in the Labrador Sea, and the subsequent mixing of Labrador Sea Water into North Atlantic Deep-Water. The long-term pattern of erosion and deep-water formation around the North Atlantic seems to have been a relatively stable feature since 1.5 Ma, although there has been a dramatic shift in the nature of physical and chemical weathering affecting the release of Hf and Pb isotopes. The modelled Nd isotopes imply a relative decrease in water mass advection into the Labrador Sea between 2.4 and 1.5 Ma, accompanied by a decrease in the rate of overturning, possibly caused by an increased freshwater input into the Labrador Sea.

Keywords: Weathering; Isotope geochemistry; Radiogenic isotopes; Glacial erosion; Argon–argon

1. Introduction

A number of radiogenic isotopes in seawater are sensitive to changes in continental weathering processes, and their changes over time offer the potential to elucidate the links between chemical weathering, consumption of atmospheric CO_2, and global temperature. Radiogenic isotopes of elements with long oceanic residence times, such as strontium, are very well mixed in the oceans and can be used to estimate long-term changes in global continental weathering because continental weathering releases Sr with high $^{87}Sr/^{86}Sr$ (e.g., Richter et al., 1992). In contrast, radiogenic isotopes with oceanic residence times similar to the mixing time of the oceans, such as neodymium (Nd), hafnium (Hf), and lead (Pb), preserve regional variations that reflect local erosional sources and their subsequent dispersal by ocean circulation (Albarede and Goldstein, 1992; von Blanckenburg et al., 1996; Albarede et al., 1998; Frank, 2002). These radiogenic

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isotopes can thus elucidate the pattern of global weathering on a regional scale. O'Nions et al. (1998) have shown that the largest changes in marine radiogenic isotope records over the past few million years have been recorded in north-western Atlantic ferromanganese crusts (detailed by Burton et al., 1999; Reynolds et al., 1999; van de Flierdt et al., 2002), rather than the Indian or Pacific Ocean records (Ling et al., 1997; O'Nions et al., 1998). These isotopic signatures in the North Atlantic are associated with the input of old continental material around the Labrador Sea and changed with the intensification of Northern Hemisphere Glaciation (NHG) (O'Nions et al., 1998; Burton et al., 1999; Reynolds et al., 1999). However, the difficulty with interpreting such isotope patterns as a simple increase in continental weathering is that changes in weathering and erosional transport processes, with glaciation, may themselves alter the radiogenic isotope signal to the oceans (von Blanckenburg and Nägler, 2001). Thus, the chemical and radiogenic isotopic records cannot be used to distinguish those changes that occur as a result of a change in weathering congruence from those caused by a change in the geographical source of material. By determining the age, and hence source, of eroded material from the physically weathered material, it is possible to estimate the radiogenic isotope composition released during the weathering of these terranes. Ar–Ar ages for detrital amphiboles have been used to estimate the Nd-isotope composition eroded into the Labrador Sea (Reynolds et al., 2004). This estimate can be directly compared to Nd-isotope data from planktonic foraminifera (Vance and Burton, 1999) from the same sediment core. In this study we use a two-box model of Nd-isotope variations to constrain the relative importance of localised weathering into the Labrador Sea and the degree of mixing of Nd into North Atlantic Deep-Water.

The Nd isotope composition of North Atlantic Deep-Water (NADW) shifted from $\varepsilon_{Nd} = -11.5$ to -13.0, between 3.0 and 2.0 Ma (Burton et al., 1999). The deep-water that forms in the Labrador Sea today has the most unradiogenic Nd-isotope composition of the global ocean due to the Archean crustal ages of the surrounding terranes. Since 2 Ma, ε_{Nd} decreased by <0.5 of an epsilon unit, but Hf isotopes decreased in ε_{Hf} by 2.5–4 epsilon units toward the present-day values (van de Flierdt et al., 2002). Pb isotopes changed on the same time scale as Hf isotopes. Thus, the radiogenic isotope records preserved by Fe–Mn crusts reveal an offset between the changes in the Nd-isotope record and those of Hf and Pb. It has been argued that the isotopic shifts reflect either changes in the source, and hence composition, of the material being eroded and transported to the Labrador Sea (Burton et al., 1999; Reynolds et al., 1999), or changes in the mineral phases being chemically weathered under glacial conditions (von Blanckenburg and Nägler, 2001). The latter hypothesis of incongruent weathering related to glacial comminution (grain-size reduction), suggests that glaciation enhances the breakdown of physically resistant minerals like zircon and provides fresh mineral surfaces for chemical weathering. These may enhance the release of unradiogenic Hf and radiogenic Pb (Piotrowski et al., 2000; van de Flierdt et al., 2002), but Nd isotopes should be less affected. Alternatively, the build-up of ice sheets may have altered the provenance of material in the Labrador Sea via changes in the mode of transport (i.e., from riverine to ice-rafted) (Winter et al., 1997) or the direction of ice-sheet movement and drainage (Bischof and Darby, 1997). It has also been argued that the middle Pleistocene transition in climate cyclicity stemmed from the grounding of ice-sheets onto the hard crystalline basement of the N. American shield (Clark and Pollard, 1998), resulting in an increased thickness of the ice-sheets and a reduction in their areal extent (Clark et al., 1999). Supporting data for this hypothesis have been found in a change in the mineral assemblages of glacial tills (Roy et al., 2004), and shifts in radiogenic isotope composition being released into seawater (Reynolds et al., 2004; Roy et al., 2004).

Whilst the oceanic isotope distribution of Nd-isotopes has been measured (e.g., Piepgras and Wasserburg, 1980), there is no data for the distribution of Pb and Hf isotopes in seawater apart from Fe–Mn crust records (von Blanckenburg et al., 1996; Albarede et al., 1998). Hence, we will focus here on Nd isotopes and estimate the continental Nd-isotope composition that is released into seawater in order to then model the subsequent mixing of the isotope composition between water masses with distinct isotope composition. This is particularly useful in the North Atlantic where there are two sites of deep-water formation that have very different Nd-isotope compositions (Fig. 1). Norwegian Sea Deep Water (NSDW) has a modern ε_{Nd} of around -10 (Lacan and Jeandel, 2004b). NSDW reaches the North Atlantic as part of Demark Strait Overflow Water (DSOW) and Iceland–Scotland Overflow Water (ISOW), which have higher ε_{Nd} values of -8.4 and -8.2, respectively (Lacan and Jeandel, 2004a,b). Labrador Sea Water (LSW) has an ε_{Nd} of about -18 (Stordal and Wasserburg, 1986; Piepgras and Wasserburg, 1987). Indeed ero-

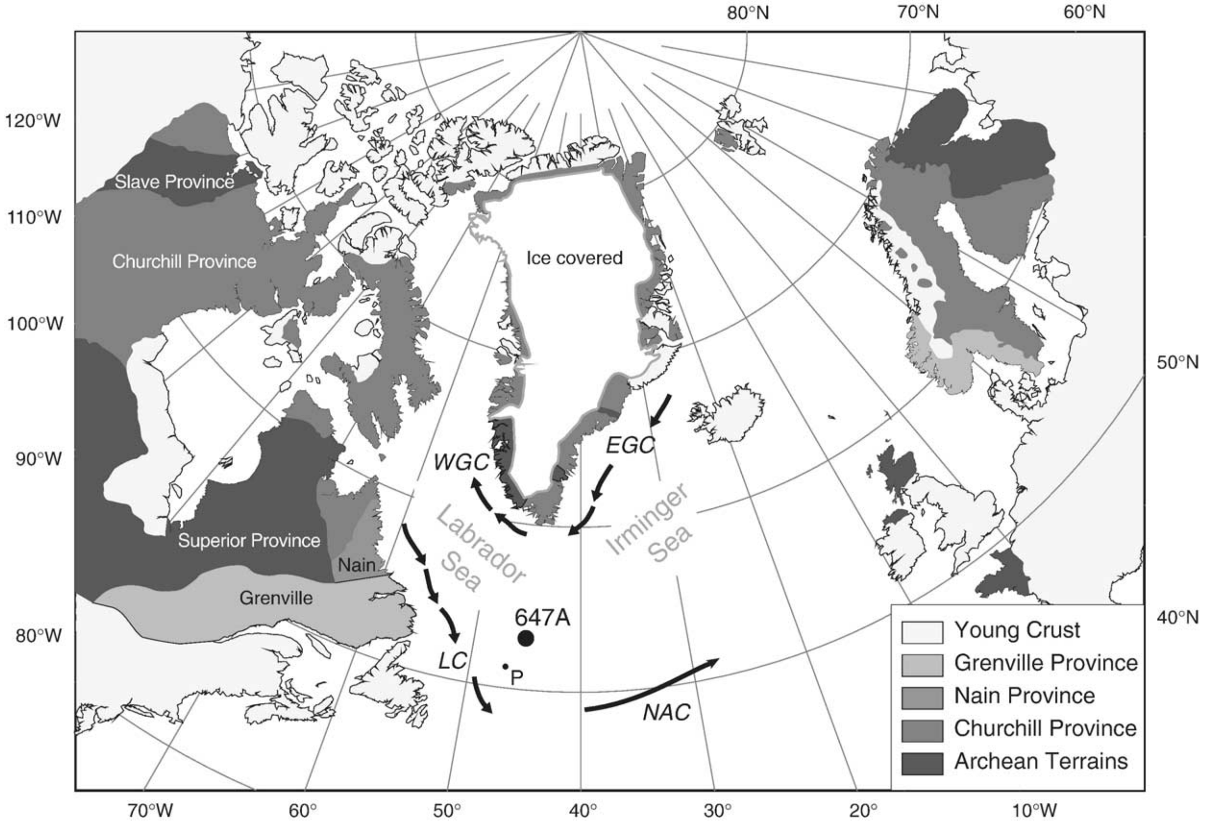

Fig. 1. The location of ODP Hole 647A in the Labrador Sea, and a Geological map of the continental areas surrounding the North Atlantic. Main geological units of different source terrains ages are shown, with darker grays for older terrains (see key). Map is based on Gwiazda et al. (1996). Point P marks the location of Station 11 from Piepgras and Wasserburg (1987) that has a surface water $\varepsilon_{\mathrm{Nd}}$ value of -17.9. Also shown are major surface water currents (NAC is the North Atlantic Current, EGC and WGC are the East and West Greenland Currents, and LC is the Labrador Current).

sional inputs into the Labrador Sea are the *only* clear source providing Nd with $\varepsilon_{\mathrm{Nd}}$ values below -11 to North Atlantic seawater.

2. Methodology

The details of Ar–Ar age determinations are given in Reynolds et al. (2004) and are summarised here in Table 1. The provenance of amphibole grains can be separated into the different source terranes around the Labrador Sea (Fig. 1), based simply on their Ar–Ar ages (based on work by Gwiazda et al., 1996; Hemming et al., 1998, 2002). The results of 255 Ar–Ar amphibole-grain ages, with individual errors of <30 Myr. or <2%, from 9 samples, shown in Fig. 2, illustrate that between 2.4 Ma and the present day, Labrador Sea detritus has been predominantly supplied from the Churchill province, and that over this time the fraction of grains from this source terrane has increased. Prior to 1.8 Ma, there was a significant component originating from the Nain and Grenville Provinces, south of the Labrador Sea. This change may be attributed to the build-up of large Northern Hemisphere ice sheets between 2.5 and 1.8 Ma. The relative amounts of amphiboles have been used to determine the relative contribution to erosion from each source terrain around the Labrador Sea. As only amphiboles from the >63 mm fraction have been used, there is a potential bias towards more localized sources as larger grains may be lost during transport. However, as the Ar–Ar results show, most of the grains do come from the Churchill Province, and are thus not locally sourced. It would thus appear that the overall distribution is not biased strongly by localized inputs, although a more localized bias in the older samples, with a larger fraction of Nain and Archean grain Ar–Ar ages, cannot be ruled out. The estimate of source terrains may also have been biased by a change in the amount of amphiboles available in the source regions, with more amphiboles being bro-

Table 1
The number of amphibole-grain analysed from ODP Hole 647A for 9 samples spanning the last 2.4 Ma, and separated into their different Ar–Ar ages: young terrains <0.6 Ga, 0.8 to 1.2 Ga from the Grenville Province, 1.2 to 1.6 Ga from the Nain Province, 1.6 to 2.1 Ga from the Churchill Province, >2.5 Ga from the Archean terrains of the Superior Province and 2.1 to 2.5 Ga that are taken to represent partially reset Archean grains from the Superior Province

Terrain:	Young	Grenville	Nain	Churchill	Superior(?)	Superior	Total	Estimated ε_{Nd} input	
Terrain Ar–Ar Age (Ga):	0.0–0.6	0.8–1.2	1.2–1.6	1.6–2.1	2.1–2.5	>2.5			
Nd-isotope composition (ε_{Nd}):	+6	−20	−24	−28	−30	−30			Adjusted with lower value for Nain
Depositional Age (Ma)	n	n	n	n	n	n		ε_{Nd} (0)	ε_{Nd} (0)
0.03	–	1	2	29	2	3	37	−28	−29
0.24	–	–	–	17	0	4	21	−28	−28
0.65	–	–	1	19	5	12	37	−29	−29
0.83	–	–	–	29	3	8	40	−29	−29
1.27	–	–	1	16	4	11	32	−29	−29
1.54	–	–	1	21	6	7	35	−29	−29
1.68	–	–	–	7	2	3	12	−29	−29
1.98	–	1	2	8	1	2	14	−27	−30
2.37	1	2	4	11	1	8	27	−26	−29

Estimated $\varepsilon_{Nd}(0)$ input is calculated using the relative fraction of grains from each terrain and the Nd isotope composition indicated, see text for details.

ken down during enhanced chemical weathering. However, as we use the relative contribution of different terrains, a regional change in the degree of chemical weathering affecting all Provinces will not affect our estimation of relative contributions.

Using an average Nd-isotope composition of each source terrain it is possible to estimate the Nd-isotope composition that was being weathered into the Labrador Sea for each time slice, see Table 1. The Ar–Ar ages cannot be used directly to estimate the Nd-isotope composition as amphiboles can be reset during metamorphism to a greater degree than the bulk Nd-isotope composition. In particular, during metamorphism in the Nain and Churchill Provinces, heating of the rocks above the Ar closure temperature of 400–500 °C reset Ar–Ar ages, whilst the Nd-isotope systematics of the bulk rocks were not strongly affected.

Estimation of the average Nd-isotope composition for large Provinces is problematic due to the large isotope variations measured, and limited data coverage. In order to avoid a biased average, as literature data are often from exotic terrains within these provinces, we have used the measured isotope composition of glacimarine and other sediments that are currently eroding around the Labrador Sea to estimate the bulk ε_{Nd} values for each Province (Farmer et al., 2003): +6 for young terrains like Iceland, −20 for the Grenville Province, −28 for the Churchill Province, −30 for the Superior Province. The ε_{Nd} value for the Grenville Province is not unambiguous, and the value we have taken is an average value measured for the Makkovikia terrane within the Grenville Province close to the Labrador Sea (Schärer, 1991; Dickin, 2000), and a composition between the ε_{Nd} values measured from sediment from the Cartwright saddle (−22) and the Gulf of St. Lawrence (−13) north and south of the Grenville Province, respectively (Farmer et al., 2003). For the Nain Province, which has young plutonic rocks and old Archean gneisses, with a range of ε_{Nd} values from −46 to +10, we have used an average ε_{Nd} value from Royse et al. (1999) of −24. Within the Nain Province the very low ε_{Nd} values of Archean Tonalites, with ε_{Nd} values from −46 to −31 (Collerson et al., 1989), are offset by Proterozoic granitoid gneiss and by amphibole rich mafic granulites. Although these values taken may not yet be fully representative, it will be shown that the model results of the Nd mass balance are relatively robust against variations in these input parameters.

The estimated Nd-isotope composition eroded into the Labrador Sea provides a tracer of continental weathering that is subsequently mixed and diluted by intra-oceanic basin mixing. The degree to which this assumed Nd-isotope composition is mixed in the Labrador Sea and then into North Atlantic Deep Water can thus be used to assess the relative contributions from other sources and the degree of mixing of water masses. We have performed a simple mass-balance for each time slice to estimate the relative proportion of Nd that is eroded from the North American Shield compared to other sources, primarily eroding in and around the Norwegian Seas. The mass-balance is based on a simple box-model shown graphically in

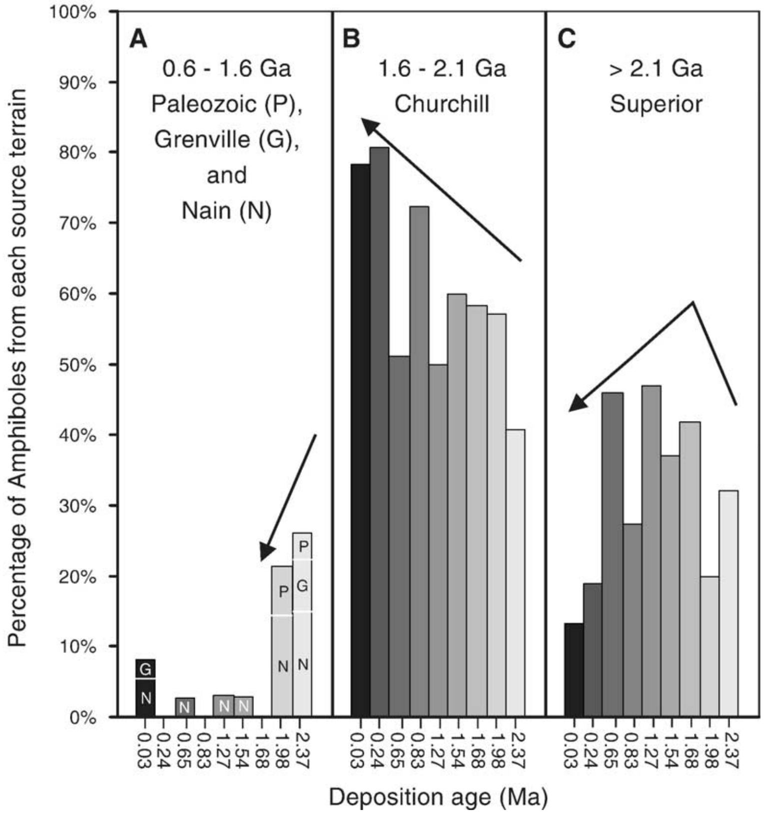

Fig. 2. The relative contribution of different source terrains, based on the amphibole-grain Ar–Ar ages for 9 samples from ODP Hole 647A spanning the last 2.4 Ma. Each of the nine samples is shown in a different grey-scale, with the stratigraphic age of the core shown below, and is split into three parts; (A) grain less than 1.6 Ga, (B) grains between 1.6 and 2.1 Ga, and (C) grains older than 2.1 Ga. Source terranes are defined as follows using the Ar–Ar ages: Paleozoic terrains (P) <0.6 Ga; Grenville Province (G) from 0.8 to 1.2 Ga; Nain Province (N) from 1.2 to 1.6 Ga; Churchill Province from 1.6 to 2.1 Ga; Superior Province with reset Archean grains 2.1 to 2.5 Ga and Archean grains >2.5 Ga.

Fig. 3. This box-model has several key assumptions that must be considered in turn:

(1) The weathered Nd-isotope composition of the source terrains does not vary over the timescale of NHG. A change in weathering environment brought about by the onset of NHG, from a chemically weathered soil covered regolith to a glacially eroded crystalline frozen basement, could have had a considerable influence on the concentration of the erosive Nd flux and potentially its isotopic composition, as is argued for changes in Pb and Hf isotopes (von Blanckenburg and Nägler, 2001; van de Flierdt et al., 2002). The Nd-isotopic composition released to solution depends on what minerals are breaking down in the soil environment, reflecting the instability of apatite and monazite (the major host phases for Nd) during weathering. Hence, under some circumstances the isotopic composition of dissolved Nd can be significantly different from that of its source rock (e.g., Andersson et al., 2001). To what extent the Nd-isotope composition can have varied due to weathering is unknown, but on a global scale there is little fractionation of Sm/Nd or $\varepsilon_{\mathrm{Nd}}$ between dissolved and particulate phases in rivers, and the Nd model ages for riverine suspended loads and source rocks are approximately equal (Goldstein and Jacobsen, 1987, 1988), and so variations due to incongruent weathering may be limited to a few $\varepsilon_{\mathrm{Nd}}$ units. It

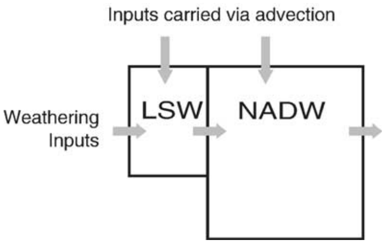

Fig. 3. Graphical representation of the box model, used for the Nd-isotope mass-balance.

will be shown that variations of this scale do not strongly affect the results. Furthermore, the foraminifera data themselves show Sm/Nd ratios close to continental values (Vance and Burton, 1999), and little variation over the past 2.5 Myr. There is a subtle shift in Sm/Nd that mirrors the change observed in ε_{Nd}, but this is not large enough to generate significant ε_{Nd} variation through incongruent weathering. Rather Sm/Nd variations reflect different sourced terrains characterized by small differences in Sm/Nd (perhaps reflecting a change in the balance of felsic vs. mafic lithologies) and large differences in ε_{Nd} values (reflecting their age). A change in the weathering environment must also be viewed in terms of relative changes between source terrains as we have not directly estimated the Nd composition from the detrital hornblende age spectra, but instead use the age spectra to define the relative contribution of different terrains.

(2) The measured Nd-isotope compositions of the planktonic foraminifera reflect a well-mixed signal of erosional and advected waters. Site 647 studied here is located in the south-eastern Labrador Sea, see Fig. 1, where the ε_{Nd} value of present-day surface waters are -17.9 (station 11; Piepgras and Wasserburg, 1987) and the youngest ε_{Nd} value record from foraminifera is -18.2 (Vance and Burton, 1999), strongly reflecting the influence of Labrador Sea surface-waters.

(3) Nd is a conservative tracer in seawater. Since the residence time of Nd in the ocean is much longer than the residence time of any water mass in the North Atlantic (von Blanckenburg and O'Nions, 1999; von Blanckenburg and Nägler, 2001; Tachikawa et al., 2003), all Nd-isotope compositions are fully transferred during water mass mixing (Lacan and Jeandel, 2004a,b,c).

(4) Deep-water in the North Atlantic is the *ONLY* significant flow of water out of the North Atlantic Subpolar Gyre, hence all the Nd released into the Labrador Sea ultimately mixes into North Atlantic Deep-Water. Labrador Sea Water (LSW) spreads out into the Irminger Sea, Iceland basin and Rockall trough (Sy et al., 1997), where the shallower levels likely form a recirculating loop within the Irminger basin and Labrador Sea and the deeper parts of the LSW are entrained into the deep-water boundary current, and ultimately NADW (McCartney, 1992; Dickson and Brown, 1994). Thus, the surface waters of the Labrador Sea do directly contribute to LSW and ultimately NADW, even if the deepwater that is actually formed is part of the subpolar gyre (Pickart et al., 2003; Lacan and Jeandel, 2004c). We use the acronyms of Labrador Sea Water (LSW) and North Atlantic Deep Water (NADW) as descriptions following von Blanckenburg and O'Nions (1999), which may approximate the modern oceanographic water masses. The model aims to describe variations at a longer time-scale than glacial–interglacial variations, and hence a fuller description of modern water masses and N. Atlantic circulation would be inappropriate.

3. Nd mass-balance

3.1. The Labrador Sea

For the Labrador Sea, the Nd-isotope composition is a mixture of continental inputs and advected inputs from Nd dissolved in the surface waters entering the Labrador Sea. The estimated Nd-isotope composition of continental input to the Labrador Sea, shown in Fig. 4a and c), shows an apparent shift at ~1.8 Ma. Since 1.8 Ma, by contrast the Nd-isotope composition of weathered input into the Labrador Sea appears to have been more or less constant, and thus reflects a constant provenance of weathered material into the Labrador Sea. We use the foraminifera ε_{Nd} records of surface water from Vance and Burton (1999), shown in Fig. 4b (and c), to reflect the mixed inputs from both weathering and advection. How the ε_{Nd} values of surface waters advected into the Labrador Sea themselves have changed over the last 3 Myrs is not known, but we can estimate its probable value given modern constraints and reasonably infer that it would have been broadly similar in the past. The East Greenland current that flows into the Labrador Sea has a modern ε_{Nd} value of -11 North of the Denmark Strait (Lacan and Jeandel, 2004a) and an ε_{Nd} value of -14 within the Subpolar Gyre (Lacan and Jeandel, 2004a). However, the lower ε_{Nd} value found south of the Demark Strait reflects a component of Nd from the Labrador Sea that has already been circulated within the Subpolar Gyre. We estimate a minimum ε_{Nd} value of -11 for the non-Labrador Sea derived component, and a maximum ε_{Nd} value of -8, which reflects the high ε_{Nd} values measured for Overflow Waters around Iceland, mentioned above (Lacan and Jeandel, 2004a,b). This Nd-isotope composition is also supported by the measured ε_{Nd} value of about -10 for clays carried in the DSOW and deposited off southern Greenland in the last 6 kyrs (Fagel et al., 2004). Assuming constant mixing in the

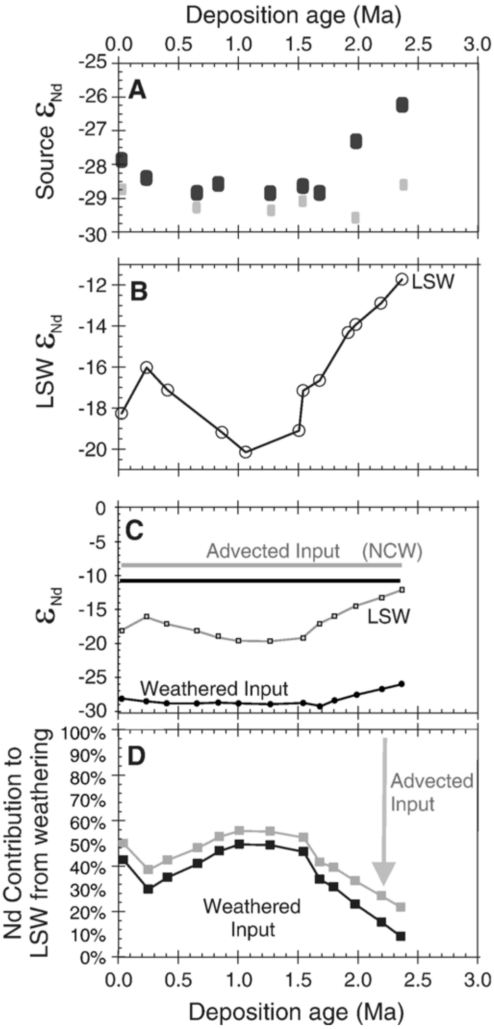

Fig. 4. (A) Estimated Nd-isotope composition of weathered inputs into the Labrador Sea based on the relative proportion of grains from each source terrane and an average isotope composition for these terranes. The model used the following ε_{Nd} values: Young terranes = +6, Grenville = −20, Nain = −24, Churchill = −28. Archean sources = −30 (See Farmer et al., 2003 and references therein), and in gray with Nain = −40. (B) Nd-isotope composition of Labrador Sea Water (LSW) recorded by planktonic foraminifera, after Vance and Burton, 1999. (C) Nd-isotope composition used in isotopic mass-balance calculations; weathered input as shown in (A), advected inputs of $\varepsilon_{Nd} = -10.8$ (in black) and $\varepsilon_{Nd} = -8.4$ (in grey), and LSW as shown in (B) in points inferred to match sampling of amphibole grains. (D) Estimated Nd contribution to LSW from the weathered input, with the remaining contribution coming from dissolved Nd advected into the Labrador Sea, with an initial composition of $\varepsilon_{Nd} = -10.8$ (in black) and $\varepsilon_{Nd} = -8.4$ (in grey).

Labrador Sea, the box-model can constrain the relative contribution of Nd in the Labrador Sea surface waters over the last 2.4 Myr. As shown in Fig. 4d, this weathered contribution increased from 9 to 46% between 2.4 and 1.5 Ma. Using a higher ε_{Nd} value of −8.4 (as observed for DSOW) for the advected input does not change the overall pattern, it simply increases the estimated continental contribution by 8–13%, as shown in grey in Fig. 4d. The change in relative contribution is obviously independent of the change in the Nd-isotope composition being eroded, and must be related to a general increase in the amount of material being eroded from the Canadian Shield during NHG and/or a decrease in the amount of Nd advected into the Labrador Sea.

An increase in the rate of deep-water production would strengthen the relative contribution of advected seawater entering the Labrador Sea, acting in the same way as a decrease in the amount of material being eroded, as seen between 1.0 and 0.3 Ma. The initiation of the Labrador Current at ~1.8 Ma (Mudie et al., 1990) might be expected to have supplied younger detrital material from East Greenland and a larger amount of Nd advected into the Labrador Sea. However, we observe the opposite, namely a decrease in the relative influences of advected Nd around this time.

The mass-balance shown in Fig. 4d is surprisingly robust to variations in the input parameters. In order for the weathered input of Nd to remain high at 2.4 Ma, using a high advected ε_{Nd} value of −9, the Nd-isotope composition of the weathered inputs (at 35%) would have to be higher than −18, about 8 ε_{Nd} values higher than our estimated input, and higher than the Nd-isotope composition of any of the surrounding terrains. Given our present understanding such a scenario would seem unlikely and hence there must have been either an increase in the erosion flux, or else a decrease in advection. This effectively rules out the possibility that the changes observed could be solely derived from incongruent weathering of Nd, as such weathering changes would not produce Nd-isotope variations of this magnitude. If the average ε_{Nd} value from the Nain Province is estimated to be much lower, say about −40, assuming the erosion of only Archean gneisses (Farmer et al., 2003), then there is no change in the Nd-isotope composition of eroded material into the Labrador Sea over the last 2.4 Myr, as shown in grey in Fig. 4a. However, this does not significantly alter the mass-balance, even for the 2.4 Ma time-slice. At this time most of the Nd in the Labrador Sea is carried in by advection and the weathered flux is small.

From mass-balance considerations, the modern erosional input of Nd to the Labrador Sea is of the same order of magnitude as the contribution from waters entering the Labrador Sea. The West Greenland Current transports about 3 Sv of water from the Nordic seas (Cuny et al., 2002). Thus the advected flux is about 3

Sv (10^6 m^3s^{-1}) of water, containing about 2.4 ppt Nd, which equates to a Nd flux of $\sim 2 \times 10^8$ g/yr. This estimated Nd flux is about half the estimated flux from volcanic arc terrains around the Pacific, and about 4% of the estimated global flux using a similar box-model approach in the North Pacific for the same time period (van de Flierdt et al., 2004). However, the total global riverine flux of Nd has been estimated to be as low as only 5×10^8 g/yr (Goldstein and Jacobsen, 1987), based on the dissolved riverine flux of the world's major rivers. This riverine based estimate has created a 'Nd paradox' (Jeandel et al., 1995), where global riverine and atmospheric fluxes of Nd are too small for the short residence time of Nd in the oceans, implying there must be an unrecognised source of Nd to the oceans. In general, additional input can be achieved in two ways: supply of dissolved Nd to the oceans through smaller rivers and streams, or additional sources within the oceans such as particle/seawater exchange. Recent work suggest that the latter effect may represent a significant contribution of Nd to the global budget (Lacan and Jeandel, 2001; Tachikawa et al., 2003), but the eroded Nd flux estimated here also implies a very significant input of Nd to the oceans from glaciated terrains around the Labrador Sea, either in the dissolved phase or released from ice-rafted particulates. This input is not considered in the global riverine fluxes due to the lack of any major river system in the area. It is not unlikely that the nature of smaller river systems and glacial discharges, without estuaries, allow for more efficient transport of the dissolved Nd into seawater. These two ways of increasing global fluxes may operate together in areas with high erosion rates that provide relatively fresh material to the ocean margins, where significant chemical weathering of marine sediments may occur via resuspension and dissolution.

3.2. North Atlantic deep water

The published records of the Nd-isotope composition of the NADW and LSW can be used to further trace the relative input of continental Nd around the Labrador Sea. Nordic waters entering the Atlantic as DSOW and ISOW entrain North Atlantic water and mix with LSW to form NADW in the modern ocean. It is unclear how this pattern has changed over the last 3 Myr, particularly during glacial conditions when deep-waters were formed further south. However, on a longer timescale, and during interglacials, this pattern of inputs of Nd from the Nordic Seas and ultimate outflow of Nd from the North Atlantic within a deep-water current may not have significantly changed. The Nd-isotope composition of NADW, as recorded by ferromanganese crusts shown in Fig. 5b, is derived from the mixing of LSW and DSOW and entrained Atlantic waters. The

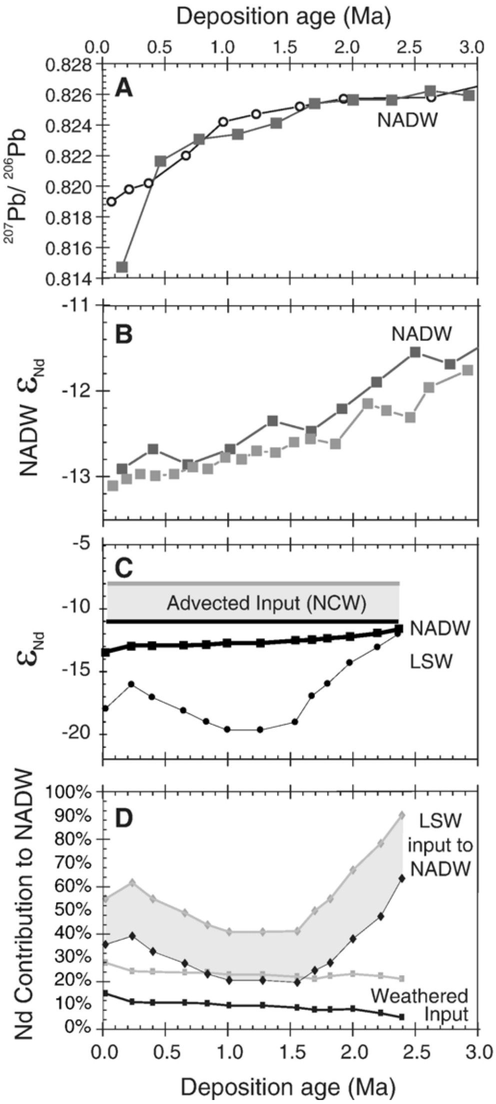

Fig. 5. (A) Comparison of $^{207}Pb/^{206}Pb$ time series of North Atlantic Deep Water (NADW) recorded by ferromanganese crusts (Burton et al., 1999; Reynolds et al., 1999). Symbols: grey squares = BM1969.05 crust, black circles = Antilles crust. (B) Nd-isotope composition of North Atlantic Deep Water (NADW) recorded by ferromanganese crusts, (Burton et al., 1999; Reynolds et al., 1999) Symbols: grey squares = BM1969.05 crust, light grey circles = Alv539 crust. (C) Nd-isotope composition used in isotopic mass-balance calculations; range of advected inputs in light grey from $\varepsilon_{Nd} = -11$ (in black) to $\varepsilon_{Nd} = -8$ (in grey), and inputs from LSW in black circles and composition of NADW in grey squares. (D) Estimated Nd contribution to NADW from LSW and the weathered input around the Labrador Sea (see Fig. 2), using a range of advected inputs in light grey from $\varepsilon_{Nd} = -11$ (in black) to $\varepsilon_{Nd} = -8$ (in grey).

Nd-isotope composition of the non-LSW endmember, including DSOW and entrained waters, is unknown, but again, taking a range of $\varepsilon_{\mathrm{Nd}}$ values between -8 and -11 should encompass all possible variations in this endmember. It seems unlikely that values would be much higher than any of the waters seen around Iceland today, or much lower given a permanent contribution to weathering from Icelandic Basalts and entrainment of waters from the Gulf Stream or North Atlantic Current with modern $\varepsilon_{\mathrm{Nd}}$ values above -11 (Piepgras and Wasserburg, 1987), with even higher values in the past as recorded by the 'Blake' ferromanganese crust (Reynolds et al., 1999). The Nd-isotope mass-balance for NADW implies a dramatic decrease in the input of LSW to NADW between 2.4 and 1.5 Ma, as shown in Fig. 5d, contemporaneous with the decrease in advected flux in the Labrador Sea shown in Fig. 4. Thus, a decrease in the advected Nd component is accompanied by a reduction in the LSW overturning rate, and may be related to a change in the amount of freshwater delivered to the Labrador Sea. The oxygen isotope data from planktonic foraminifera in the Labrador Sea do not show a major change until ~1.5 Ma, when there is an abrupt increase in the δ^{18}O record (Aksu et al., 1989; Vance and Burton, 1999).

The oceanographic water-mass estimates of the Labrador Sea Water component of NADW vary from inputs of 2 to 4 Sv out of a total deep-water export of ~14 Sv, or 15 to 30% (see Dickson and Brown, 1994). The modern Nd contribution we estimate (36%) is close to the volumes estimated above, given that LSW has an enhanced Nd concentration due to the additional weathering inputs.

The Nd-isotope mass-balance calculations are surprisingly robust to the choice of values taken for the $\varepsilon_{\mathrm{Nd}}$ value of waters mixing with LSW to form NADW. Only if the $\varepsilon_{\mathrm{Nd}}$ value of the non-LSW endmember is below -11.5 could the overturning in LSW prior to 2 Ma not have been higher than modern day. There is no obvious source to provide such an unradiogenic endmember, that could alter the more radiogenic composition of the Gulf Stream, as recorded in Fe–Mn crust on the Blake Plateau at 2.5 Ma ($\varepsilon_{\mathrm{Nd}}=-9.7$, (Reynolds et al., 1999), or the modern East Greenland Current ($\varepsilon_{\mathrm{Nd}}=-10.8$ (Lacan and Jeandel, 2004a,b). This does not imply that there were no terrains eroding around the North Atlantic that have a more unradiogenic Nd isotope composition than -11 $\varepsilon_{\mathrm{Nd}}$ units, but that given the strong effect of the Icelandic Tertiary volcanism region on the modern composition of waters around Iceland ((Lacan and Jeandel, 2004a,b), it seems unlikely that Norwegian or Appalachians sources of older crustal material could provide the amount of dissolved Nd required to balance the Nd-isotope composition in the Labrador Sea. The only conceivable source would be significant erosion of Archean material from Greenland eastwards into the East Greenland current prior to the build-up of the permanent ice-sheet now over Greenland. Again, this would imply that the change in the distribution of weathering and delivery of freshwater has changed the rate of overturning and the observed marine Nd-isotope composition.

As all the local inputs of Nd to LSW are effectively carried into the North Atlantic (von Blanckenburg and Nägler, 2001), and the total Nd contribution to NADW from weathered material around the Labrador Sea barely doubled (Fig. 5d), the amount of erosion to the Labrador Sea cannot have risen dramatically (much more than two-fold). This argument would imply that the change in Nd contribution shown in Fig. 4 is principally governed by a decrease in advection, rather than a simple increase in erosion around the Labrador Sea alone. This reduction in advection and water overturn since the onset of NHG agrees with mass-balance calculations for Nd isotopes between NADW and the Southern Ocean (Frank et al., 2002).

4. Conclusions

Simple mass-balance calculations imply that changes in the Nd-isotope composition of LSW and NADW, between 2.5 and 1.5 Ma, reflect both an increase in erosion and a decrease in the amount of advection and deep-water formation in the Nordic Seas and within the Labrador Sea itself. This conclusion does not neglect the smaller affect of a change in the source of material being eroded, principally a cessation of the erosion of material younger than 1.6 Ga. The reduction in deep-water formation occurred contemporaneously with a change in the nature of erosion around the Laurentide ice sheet at 1.8 Ma (McIntyre et al., 1999; Winter et al., 1997). The ice-sheet may have modified the hydrological cycle and the location of freshwater input around the North Atlantic. The long-term pattern of erosion and deep-water formation around the North Atlantic seems to have been a relatively constant feature since 1.5 Ma, although the effects of glacial–interglacial changes cannot be resolved in this study. Major changes in the Pb and Hf isotope compositions in the northwest Atlantic occurred since 1.5 Ma, significantly later than changes in the Nd isotopes, and are more likely to have been caused by a change in the nature of the weathering process and the degree of physical and chemical weathering.

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References

Aksu, A.E., de Vernal, A., Mudie, P.J., 1989. High-resolution foraminifer, palynologic and stable isotopic records of upper Pleistocene sediments from the Labrador Sea: paleoclimatic and paleoceanographic trends. Proc. Ocean Drill. Program 105B, 617–652.

Albarede, F., Goldstein, S.L., 1992. World map of Nd isotopes in seafloor ferromanganese deposits. Geology 20, 761–763.

Albarede, F., Simonetti, A., Vervoort, J.D., Blichert-Toft, J., Abouchami, W., 1998. A Hf–Nd isotopic correlation in ferromanganese nodules. Geophys. Res. Lett. 25, 3895–3898.

Andersson, P.S., Dahlqvist, R., Ingri, J., Gustafsson, O., 2001. The isotopic composition of Nd in a boreal river: a reflection of selective weathering and colloidal transport. Geochim. Cosmochim. Acta 65 (4), 521–527.

Bischof, J.F., Darby, D.A., 1997. Mid-to late Pleistocene ice drift in the western Arctic Ocean: evidence for a different circulation in the past. Science 277, 74–78.

Burton, K.W., Lee, D.C., Christensen, J.N., Halliday, A.N., Hein, J.R., 1999. Actual timing of neodymium isotopic variations recorded by Fe–Mn crusts in the western North Atlantic. Earth Planet. Sci. Lett. 171, 149–156.

Clark, P.U., Pollard, D., 1998. Origin of the middle pleistocene transition by ice sheet erosion of regolith. Paleoceanography 13, 1–9.

Clark, P.U., Alley, R.B., Pollard, D., 1999. Climatology—northern hemisphere ice-sheet influences on global climate change. Science 286 (5442), 1104–1111.

Collerson, K.D., McCulloch, M.T., Nutman, A.P., 1989. Sr-isotope and Nd-isotope systematics of polymetamorphic archean gneisses from southern west Greenland and Northern Labrador. Can. J. Earth Sci. 26 (3), 446–466.

Cuny, J., Rhines, P.B., Niiler, P.P., Bacon, S., 2002. Labrador sea boundary currents and the fate of the Irminger Sea Water. J. Phys. Oceanogr. 32 (2), 627–647.

Dickin, A.P., 2000. Crustal formation in the Grenville province: Nd-isotope evidence. Can. J. Earth Sci. 37 (2), 165–181.

Dickson, R.R., Brown, J., 1994. The production of North Atlantic deep water: sources, rates and pathways. J. Geophys. Res. 99 (C6), 12319–12341.

Fagel, N., Hillaire-Marcel, C., Humblet, M., Brasseur, R., Weis, D., Stevenson, R., 2004. Nd and Pb isotope signatures of the clay-size fraction of Labrador Sea sediments during the holocene: implications for the inception of the modern deep circulation pattern. Paleoceanography 19, PA3002, doi:10.1029/2003PA000993.

Farmer, G.L., Barber, D., Andrews, J., 2003. Provenance of late quaternary ice-proximal sediments in the North Atlantic: Nd, Sr and Pb isotopic evidence. Earth Planet. Sci. Lett. 209, 227–243.

Frank, M., 2002. Radiogenic isotopes: tracers of past ocean circulation and erosional input. Rev. Geophys. 40 (1), doi:10.1029/2000RG000094.

Frank, M., Whiteley, N., Kasten, S., Hein, J.R., O'Nions, K., 2002. North Atlantic deep water export to the southern Ocean over the past 14 Myr: evidence from Nd and Pb isotopes in ferromanganese crusts. Paleoceanography 17 (2), doi:10.1029/2000PA000606.

Goldstein, S.L., Jacobsen, S.B., 1987. The Nd and Sr isotopic systematics of river-water dissolved material: implications for the sources of Nd and Sr in seawater. Chem. Geol. 66, 245–272.

Goldstein, S.L., Jacobsen, S.B., 1988. Nd and Sr isotopic systematics of river water suspended material implications for crustal evolution. Earth Planet. Sci. Lett. 87, 249–265.

Gwiazda, R.H., Hemming, S.R., Broecker, W.S., Onsttot, T., Mueller, C., 1996. Evidence from Ar-40/Ar-39 ages for a Churchill province source of ice-rafted amphiboles in Heinrich layer 2. J. Glaciol. 42, 440–446.

Hemming, S.R., Broecker, W.S., Sharp, W.D., Bond, G.C., Gwiazda, R.H., McManus, J.F., et al., 1998. Provenance of Heinrich layers in core V28-82, northeastern Atlantic: Ar-40/Ar-39 ages of ice-rafted hornblende, Pb isotopes in feldspar grains, and Nd–Sr–Pb isotopes in the fine sediment fraction. Earth Planet. Sci. Lett. 164, 317–333.

Hemming, S.R., Hall, C.M., Biscaye, P.E., Higgins, S.M., Bond, G.C., McManus, J.F., et al., 2002. Ar-40/Ar-39 ages and Ar-40* concentrations of fine-grained sediment fractions from North Atlantic Heinrich layers. Chem. Geol. 182, 583–603.

Jeandel, C., Bishop, J.K., Zindler, A., 1995. Exchange of Neodymium and its isotopes between seawater and small and large particles in the Sargasso Sea. Geochim. Cosmochim. Acta 59 (3), 535–547.

Lacan, F., Jeandel, C., 2001. Tracing Papua New Guinea imprint on the central equatorial Pacific Ocean using neodymium isotopic compositions and rare Earth element patterns. Earth Planet. Sci. Lett. 186 (3–4), 497–512.

Lacan, F., Jeandel, C., 2004a. Denmark strait water circulation traced by heterogeneity in neodymium isotopic compositions. Deep-Sea Res., Part I, Oceanogr. Res. Pap. 51, 71–82.

Lacan, F., Jeandel, C., 2004b. Neodymium isotopic composition and rare earth element concentrations in the deep and intermediate Nordic Seas: constraints on the Iceland Scotland overflow water signature. Geochem. Geophys. Geosyst. 5 (11), Q11006, doi:10.1029/2004GC000742.

Lacan, F., Jeandel, C., 2004c. Subpolar mode water formation traced by neodymium isotopic composition. Geophys. Res. Lett. 31, L14306, doi:10.1029/2004GL019747.

Ling, H., Burton, K., O'Nions, R., Kamber, B., von Blanckenburg, F., Gibb, A., et al., 1997. Evolution of Nd and Pb isotopes in central Pacific seawater from ferromanganese crusts. Earth Planet. Sci. Lett. 146, 1–12.

McCartney, M.S., 1992. Recirculating components to the deep boundary current of the northern North-Atlantic. Prog. Oceanogr. 29 (4), 283–383.

McIntyre, K., Ravelo, A.C., Delaney, M.L., 1999. North Atlantic intermediate waters in the late Pliocene to early Pleistocene. Paleoceanography 14, 324–335.

Mudie, P.J., DeVernal, A., Head, M.J., 1990. Neogene to recent palynostratigraphy of circum-arctic basins: results of ODP leg 104, norwegian sea, leg 105, Baffin Bay, and DSDP site 611, Irminger Sea. In: Bleil, U., Theide, J. (Eds.), Geological History of the Polar Oceans: Artic versus Antartic. Kluwer Academic Pulishers.

O'Nions, R.K., Frank, M., von Blanckenburg, F., Ling, H.-F., 1998. Secular variation of Nd and Pb isotopes in ferromanganese crusts from the Atlantic, Indian and Pacific Oceans. Earth Planet. Sci. Lett. 155, 15–28.

Pickart, R.S., Straneo, F., Moore, G.W.K., 2003. Is Labrador sea water formed in the Irminger basin? Deep-Sea Res., Part I, Oceanogr. Res. Pap. 50 (1), 23–52.

Piepgras, D.J., Wasserburg, G.J., 1980. Neodymium isotopic variations in seawater. Earth Planet. Sci. Lett. 50 (1), 128–138.

Piepgras, D.J., Wasserburg, G.J., 1987. Rare earth element transport in the western North Atlantic inferred from Nd isotopic observations. Geochim. Cosmochim. Acta 51 (5), 1257–1271.

Piotrowski, A.M., Lee, D.C., Christensen, J.N., Burton, K.W., Halliday, A.N., Hein, J.R., et al., 2000. Changes in erosion and ocean circulation recorded in the Hf isotopic compositions of North Atlantic and Indian Ocean ferromanganese crusts. Earth Planet. Sci. Lett. 181 (3), 315–325.

Reynolds, B.C., Frank, M., O'Nions, R.K., 1999. Nd and Pb isotope time series from Atlantic ferromanganese crusts: implications for changes in provenance and paleocirculation over the last 8 Ma. Earth Planet. Sci. Lett. 173, 381–396.

Reynolds, B.C., Sherlock, S.C., Kelley, S.P., Burton, K.W., 2004. Radiogenic isotope records of quaternary glaciations: changes in the erosional source and weathering processes. Geology 32 (10), 861–864.

Richter, F.M., Rowley, D.B., Depaolo, D.J., 1992. Sr isotope evolution of seawater — the role of tectonics. Earth Planet. Sci. Lett. 109 (1–2), 11–23.

Roy, M., Clark, P.U., Raisbeck, G.M., Yiou, F., 2004. Geochemical constraints on the regolith hypothesis for the middle Pleistocene transition. Earth Planet. Sci. Lett. 227 (3–4), 281–296.

Royse, K.R., Noble, S.R., Tarney, J., Cadman, A.C., 1999. Country-rock contamination of marginal mafic granulites bordering the Nain Plutonic Suite: implications for mobilization of Sr during high-grade contact metamorphism. Can. J. Earth Sci. 36 (6), 985–997.

Schärer, U., 1991. Rapid continental-crust formation at 1.7 Ga from a Reservoir with chondritic isotope signatures, eastern Labrador. Earth Planet. Sci. Lett. 102 (2), 110–133.

Stordal, M.C., Wasserburg, G.J., 1986. Neodymium isotopic study of Baffin Bay water; sources of REE from very old terranes. Earth Planet. Sci. Lett. 77 (3–4), 259–272.

Sy, A., Rhein, M., Lazier, J.R.N., Koltermann, K.P., Meincke, J., Putzka, A., et al., 1997. Surprisingly rapid spreading of newly formed intermediate waters across the North Atlantic ocean. Nature 386 (6626), 675–679.

Tachikawa, K., Athias, V., Jeandel, C., 2003. Neodymium budget in the modern ocean and paleo-oceanographic implications. J. Geophys. Res. 108 (C8), 3254.

Vance, D., Burton, K.W., 1999. Neodymium isotopes in planktonic foraminifera: a record of the response of continental weathering and ocean circulation rates to climate change. Earth Planet. Sci. Lett. 173, 365–379.

van de Flierdt, T., Frank, M., Lee, D.C., Halliday, A.N., 2002. Glacial weathering and the hafnium isotope composition of seawater. Earth Planet. Sci. Lett. 198, 167–175.

van de Flierdt, T., Frank, M., Lee, D.-C., Halliday, A.N., Reynolds, B.C., Hein, J.R., 2004. New constraints on the sources and behavior of neodymium and hafnium in seawater from Pacific Ocean ferromanganese crusts. Geochim. Cosmochim. Acta 68, 3827–3843.

von Blanckenburg, F., Nägler, T.F., 2001. Weathering versus circulation-controlled changes in radiogenic isotope tracer composition of the Labrador Sea and North Atlantic deep water. Paleoceanography 16, 424–434.

von Blanckenburg, F., O'Nions, R.K., 1999. Response of beryllium and radiogenic isotope ratios in northern Atlantic Deep Water to the onset of northern Hemisphere glaciation. Earth Planet. Sci. Lett. 167, 175–182.

von Blanckenburg, F., O'Nions, R.K., Hein, J.R., 1996. Distribution and sources of pre-anthropogenic lead isotopes in deep ocean water from Fe–Mn crusts. Geochim. Cosmochim. Acta 60, 4957–4963.

Winter, B., Johnson, C.M., Clark, D.L., 1997. Strontium, neodymium and lead isotope variations of authigenic silicate sediment components from the late Cenozoic Arctic Ocean. Implications for sediment provenance and the source of trace metals in sea water. Geochim. Cosmochim. Acta 60, 4957–4963.