ABSTRACT

The neodymium isotopic composition of authigenic phases of deep-sea sediment cores can be interpreted as reflecting past changes in water-mass mixing proportions if end-member water-mass compositions are constrained through time. Here we present three new records spanning 2480 to 4360 m depth in the North Atlantic Ocean that show seawater Nd isotope values in the early to mid-Holocene that are more radiogenic than values from the abyssal northwest Atlantic. This finding indicates that the end-member composition of North Atlantic Deep Water was more stable within its core than it was at abyssal depths. The spatial distribution of the unradiogenic neodymium isotope values observed in the North Atlantic suggests a bottom source, and therefore that they were unlikely to have been due to the production of intermediate-depth Labrador Sea Water. We infer that the unradiogenic authigenic Nd isotope values were most likely derived from a pulse of poorly chemically weathered detrital material that was deposited into the Labrador Sea following Laurentide ice sheet retreat in the early Holocene. This unradiogenic sediment released neodymium into the bottom waters, yielding an unradiogenic seawater signal that was advected southward at abyssal depths and attenuated as it vertically mixed upward in the water column to shallower depths. The southward dispersion of these unradiogenic seawater values traces deep-water advection. However, the exact values observed at the most abyssal sites cannot be interpreted as proportional to the strength of deep-water production without improved constraints on end-member changes.

INTRODUCTION

Changes in North Atlantic Deep Water (NADW) production, inferred from paleocceanographic proxy evidence, are thought to be integral to past changes in the climate (Roberts et al., 2010). One such proxy is the neodymium isotopic composition of seawater that has been shown to trace the distribution of water masses in the Atlantic Ocean (Lambelet et al., 2016). The characteristic \( \varepsilon_{\text{Nd}} \) values \( \varepsilon_{\text{Nd}} = \left( \frac{^{143}\text{Nd}/^{144}\text{Nd}_{\text{sample}}}{^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}} - 1 \right) \times 10,000 \), where \( ^{144}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}} = 0.512638 \) (CHUR—chondritic uniform reservoir; Jacobsen and Wasserburg, 1980)) of NADW in the modern Atlantic reflect the mixing of more radiogenic deep overflow waters from the Nordic Seas (\( \varepsilon_{\text{Nd}} \) of −11.8 to −12.5) and less radiogenic intermediate-depth water from the Labrador Sea (\( \varepsilon_{\text{Nd}} \) of −13.7 to −14.2) (Lambelet et al., 2016).

The authigenic phases of seafloor sediment cores have been used to infer changes in seawater \( \varepsilon_{\text{Nd}} \), and thus water-mass mixing and NADW production, in the past (e.g., Gutjahr et al., 2008; Roberts et al., 2010; Crocket et al., 2011; Böhm et al., 2015; Lippold et al., 2016). This interpretation is complicated by studies based on the Bermuda Rise in the abyssal northwestern Atlantic that have found \( \varepsilon_{\text{Nd}} \) values that are more negative than the modern composition of NADW during warm climate periods with values as low as −16.2 in the early to mid-Holocene (Roberts et al., 2010), −16.0 during the interstadials of Marine Isotope Stage (MIS) 3, and −18.3 during MIS 5 (Böhm et al., 2015). Such extreme unradiogenic values have been hypothesized to represent changes in the relative proportions of different northern-sourced water masses, for example, greater production of unradiogenic Labrador Sea Water (LSW) (Roberts et al., 2010; Böhm et al., 2015) or to correspond to stronger NADW production (Lippold et al., 2016). Alternatively, these values may have been caused by input processes that modified the Nd isotopic end-member composition of NADW independent of changes in deep-water production, such as the drainage of Lake Agassiz (North America) during the 8.2 ka event (Crocket et al., 2011).

The spatial extent of these unradiogenic neodymium isotope values is poorly constrained, especially at intermediate to mid-depths. High-resolution Fe-Mn crust records from 1800 and 2000 m depth in the North Atlantic display stable \( \varepsilon_{\text{Nd}} \) values across the past 500 k.y. (Foster et al., 2007), but do not afford the same resolution as records from sediment cores. Given that the southward flux of NADW is stronger at intermediate to mid-depths (1000–3000 m) than in the abyssal Atlantic (Kuhlbrodt et al., 2007), placing constraints on the vertical distribution of the \( \varepsilon_{\text{Nd}} \) values in the North Atlantic during warm periods is essential to correctly determining the relationship of \( \varepsilon_{\text{Nd}} \) to Atlantic overturning circulation.

In this work we present foraminiferal \( \varepsilon_{\text{Nd}} \) records of the past 23 k.y. from 3 sites (core SU90-03, on the Mid-Atlantic Ridge at 40.0°N, 32.0°W, 2480 m; from the PALEOCINAT cruise, R/V Le Suroît; Ocean Drilling Program [ODP] Site 925E, 4.2°N, 43.5°W, 3040 m; and ODP Site 929B, on the Ceara Rise in the equatorial western Atlantic, 6.0°N, 43.7°W, 4360 m) that span from 2480 to 4360 m depth in the Atlantic (Fig. 1), to provide new constraints on the spatial extent of the unradiogenic \( \varepsilon_{\text{Nd}} \) values observed in the North Atlantic in the early Holocene (Gutjahr et al., 2008; Colin et al., 2010; Roberts et al., 2010; Crocket et al., 2011; van de Flierdt et al., 2006; Lippold et al., 2016). This allows us to address both the source of those unradiogenic Nd isotope values during the Holocene and the temporal and spatial stability of the NADW end member through time.

METHODS

We measured \( \varepsilon_{\text{Nd}} \) on chemically uncleaned planktic foraminifera from the past 23 k.y. at 3 sites: SU90-03, ODP Site 925E, and ODP Site 929B (Fig. 1). The age models of all three cores were presented elsewhere (Chapman and Shackleton, 1998; Howe et al., 2016). The SU90-03 core site and ODP Site 925E are bathed predominantly by NADW in the modern ocean, whereas ODP Site 929B is near the boundary of NADW and Antarctic Bottom Water (AABW) (Fig. 1). Samples were prepared and analyzed following the methods of Roberts et al. (2010), who showed that planktic foraminifera yield bottom-water \( \varepsilon_{\text{Nd}} \) values. Isotopic measurements were made on Nu Plasma and NeptunePlus multicollector–inductively coupled plasma–mass spectrometers at the University of Cambridge (UK). Measurements were corrected to a \( ^{144}\text{Nd}/^{144}\text{Nd} \) ratio of 0.7219. Samples were bracketed with concentration matched solutions of standard NDi-1 that were corrected to the accepted \( ^{144}\text{Nd}/^{144}\text{Nd} \) ratio of 0.512115 (Tanaka et al., 2000). All errors reported are the \( \pm \) external error of the bracketing standards unless the internal error of a given
RESULTS
The foraminiferal eNd records from core SU90-03, ODP 925E, and ODP 929B are most radiogenic during the Last Glacial Maximum (LGM) and least radiogenic during the early to mid-Holocene (11–4 ka) (Fig. 2B), for simplicity referred to herein as early Holocene. The unradiogenic values in the early Holocene are followed by shifts to more radiogenic values, creating an unradiogenic early Holocene peak in all three records. The SU90-03 (2480 m) record is very similar to the authigenic eNd record from the deep Bermuda Rise (4540 m; Fig. 2B), except that its early Holocene peak is significantly more radiogenic (eNd = -13.5) than that of the deep Bermuda Rise site (eNd = -16.2) (Roberts et al., 2010).

During the LGM, ODP Sites 925E and 929B from the equatorial Atlantic (light gray triangles and dark gray diamonds in Fig. 2B) display more radiogenic eNd values, and therefore a greater proportion of southern-sourced water (Howe et al., 2016), than the two more northern sites. In contrast, during the Holocene ODP 925E displays slightly less radiogenic values than that of SU90-03, although this offset is within the bounds of analytical error. This similarity demonstrates that throughout the Holocene, ODP Site 925E and the core SU90-03 site were bathed by a similar water mass. That ODP 929B is consistently offset to more radiogenic values than the other sites (Fig. 2B) indicates that it was bathed by a greater proportion of more radiogenic, southern-sourced water.

DISCUSSION
The unradiogenic early Holocene peak found in all five Atlantic records (Fig. 2B) implies that there was a source of unradiogenic neodymium during the early Holocene that is no longer active in the modern ocean. This source did not, however, affect all depths of the Atlantic equally (Fig. 2B). Both the SU90-03 core site (2480 m) and ODP Site 925E (3040 m) are predominantly bathed by northern-sourced water in the modern ocean (Fig. 1). These sites were also bathed by northern-sourced water during the early Holocene, as indicated by their benthic foraminiferal d13C records (Fig. DR1 in the GSA Data Repository1). This inference, combined with published early Holocene eNd data from the North Atlantic (Fig. 3), reveals that the eNd of NADW at mid-depths during the

1GSA Data Repository item 2016272, Figure DR1 (deglacial foraminiferal carbon isotope records from the North Atlantic); Figure DR2 (foraminiferal and detrital neodymium isopes from the Bermuda Rise); foraminiferal Nd isotope data from core SU90-03, ODP Site 925E, and ODP Site 929B; least radiogenic authigenic Nd isotope data from the North Atlantic in the early to mid-Holocene; and radiocarbon dates of ODP Site 925E and ODP Site 929B, is available online at www.geosociety.org/pubs/ft2016.htm, or on request from editing@geosociety.org.
early Holocene was only $-13.5$ to $-14.5$. The large unradiogenic end-member shift observed at the Bermuda Rise was clearly restricted to the most abyssal parts of the North Atlantic.

This conclusion argues against the hypothesis that the unradiogenic values at the Bermuda Rise during warm periods were due to a greater proportion of LSW (Roberts et al., 2010; Böhm et al., 2015). In the modern ocean, LSW, with its characteristic unradiogenic signature, is formed by open-ocean convection in the Labrador Sea and is less dense than the more radiogenic overflow waters from the Nordic Seas, thus is more prevalent at intermediate to mid-depths than in the abyssal Atlantic (Talley and McCartney, 1982; Lambelet et al., 2016). Reconstructions based upon foraminiferal stable isotopes have shown that this water-mass structure was stable throughout the Holocene (Hillaire-Marcel and Bilodeau, 2000). Therefore, if the unradiogenic values observed at the Bermuda Rise were due to LSW formation, equally or even more unradiogenic waters should have bathed mid-depth core sites such as SU90-03 during the early Holocene. Instead, the unradiogenic early Holocene seawater $e_{\text{Nd}}$ values at abyssal depths (Fig. 3) must have had a bottom-derived source.

Although we have discounted the water mass LSW as the source of unradiogenic Nd to the Bermuda Rise, the sediments of the Labrador Sea have been noted as a source of neodymium to bottom waters in the modern Labrador Sea (Lacan and Jeandel, 2005). Following the retreat of Northern Hemisphere ice sheets across the deglaciation, a large area of poorly chemically weathered bedrock would be freshly exposed (Blum, 1997). The weathering products of the unradiogenic Canadian shield enter the North Atlantic via the Labrador Sea (Fagel et al., 1999), with the detrital fraction of cores in this region displaying $e_{\text{Nd}}$ values as unradiogenic as $-24$ during the early Holocene (Fig. 2A). If a large pulse of poorly chemically weathered sediment of such an unradiogenic composition was delivered to the bottom of the Labrador Sea in the early Holocene, this would have been reactive for boundary exchange, leading to the re-labeling of the deep western boundary current in the northwest Atlantic with unradiogenic neodymium (von Blankenburg and Nügler, 2001).

It is important to note that we interpret the unradiogenic values to reflect an abyssal water mass rather than the signature of a local pore-water process at the Bermuda Rise site. This is because a depth transect from 30°N to 40°N in the Atlantic in the early Holocene (Figs. 2B and 3) shows a clear neodymium isotopic gradient with depth, where the least radiogenic value is observed at the greatest depth ($-16.2$ at 4540 m), intermediate values ($-14.3$ and $-14.6$) occur from 3400 to 4250 m, and the most radiogenic value is seen in the core of NADW ($-13.5$ at 2450 m). This suggests that a distinct chemical water mass was present at abyssal depths in the western North Atlantic during the early Holocene, and that its composition was mixed upward and attenuated with the core of NADW.

A further argument against pore-water control is that reductively cleaned fish debris and both chemically cleaned and uncleaned foraminifera from the deep Bermuda Rise site all record the same unradiogenic values of $-16.2$ in the early Holocene (Roberts et al., 2010). If incorporation of the Nd isotope signal occurred in differing bottom and pore waters, then differential chemical cleaning would be expected to remove some of the diagenetically overprinted signal. As a result, the Nd isotope values of the reductively cleaned foraminifera should diverge from those that had not been cleaned of coatings, and should also diverge from the fish teeth. Such divergence is not, however, observed (Roberts et al., 2010), indicating that pore-water neodymium is not overprinting the bottom-water composition preserved at that site. Furthermore, the foraminiferal and detrital $e_{\text{Nd}}$ values of the deep Bermuda Rise site (Fig. DR2) are strongly decoupled during both the LGM and, important for this study, the late Holocene. The trend of detrital values through time shows the Bermuda Rise site becoming less radiogenic during the Holocene when foraminiferal values become more radiogenic; this observation argues strongly that the early Holocene unradiogenic peak in the foraminiferal record is not an artifact of the detrital composition.

Coral results from the intermediate-depth northeast Atlantic show values as unradiogenic as $-15.4$ in the early Holocene (Colin et al., 2010). This suggests that unradiogenic neodymium sediment deposited into the Labrador Sea during the early Holocene may have also added very unradiogenic dissolved neodymium to shallow and intermediate-depth water in the Labrador Sea that was subsequently mixed into the northeast Atlantic at intermediate depths (Colin et al., 2010). This may also have been the cause of the unradiogenic values in intermediate-depth corals in the northwest Atlantic in the earliest Holocene (van de Flierdt et al., 2006). These unradiogenic values are consistent with the preferential release of unradiogenic neodymium during weathering (von Blankenburg and Nügler, 2001). Some of this unradiogenic surface water could also have been entrained into NADW production, thereby explaining the muted early Holocene peak observed at mid-depths in the North Atlantic (2.5–4.3 km; Figs. 2 and 3). Alternatively, this muted peak might represent a diapycnally mixed signal from the unradiogenic chemical water mass at >4.5 km depths. However, it is clear that the end-member composition of NADW was only slightly changed by this input and must have been buffered by a large volume of NADW forming with $e_{\text{Nd}}$ values similar to today, likely in the Nordic Seas.

The mechanism that generated unradiogenic $e_{\text{Nd}}$ peaks at the deep Bermuda Rise appears to be unique to warm periods (Böhm et al., 2015). Although unradiogenic peaks are seen during Heinrich Stadial 1 (HS1) in a detrital neodymium record from the Labrador Sea (Fig. 2A) and in a few cores directly within the Ruddiman ice-rafting debris belt (U1313; Fig. 2B) (Roberts and Piotrowski, 2015), there is little evidence for unradiogenic Nd isotope peaks during Heinrich events in the authigenic Nd records from further south in the North Atlantic (Fig. 2B). Despite the large amount of ice-rafted debris deposited in the North Atlantic during HS1 (Hemming, 2004), a chemical signal derived from this material clearly was not propagated to the deep northwest Atlantic. These observations suggest that both the retreat of the Laurentide Ice Sheet...
poorly chemically weathered sediment into the Labrador Sea and strong southward advection of modified deep water out of the Labrador Sea are required to cause radiogenic seawater $\varepsilon_{Nd}$ values at the deep Bermuda Rise. However, coral measurements from intermediate depths near the Bermuda Rise show radiogenic values typical of LSW during HS1 (Wilson et al., 2014), consistent with the sustained southward export of northern-sourced water at intermediate depths during HS1 (Bradtmiller et al., 2014).

Therefore, we conclude that the radiogenic values at the deep Bermuda Rise are indicative of Atlantic overturning and southward deep-water export during the Holocene; however, the exact $\varepsilon_{Nd}$ values cannot be taken as proportionate to the strength of deep-water production due to as-yet unconstrained source changes. The restriction of these extreme radiogenic values to the most abyssal (~4500 m depth; Fig. 3) northwest Atlantic during the early Holocene (Fig. 3), however, indicates that the $\varepsilon_{Nd}$ of the NADW end member as a whole was relatively more stable (Foster et al., 2007) than records from the Bermuda Rise sites suggest (Roberts et al., 2010). The mechanism proposed here may also explain the radiogenic values observed at the Bermuda Rise during other warm periods (Böhm et al., 2015), although mid-depth Atlantic records for those periods would increase certainty. Notwithstanding this uncertainty, we conclude that neodymium isotopes remain a viable proxy for reconstructing past changes in water-mass mixing when underpinned by spatial constraints of end-member values.

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