The Impact of Benthic Processes on Rare Earth Element and Neodymium Isotope Distributions in the Oceans

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Neodymium (Nd) isotopes are considered a valuable tracer of modern and past ocean circulation. However, the promise of Nd isotope as a water mass tracer is hindered because there is not an entirely self-consistent model of the marine geochemical cycle of rare earth elements (REEs, of which Nd is one). That is, the prevailing mechanisms to describe the distributions of elemental and isotopic Nd are not completely reconciled. Here, we use published [Nd] and Nd isotope data to examine the prevailing model assumptions, and further compare these data to emergent alternative models that emphasize benthic processes in controlling the cycle of marine REEs and Nd isotopes. Our conclusion is that changing from a "top-down" driven model for REE cycling to one of a "bottom-up" benthic source model can provide consistent interpretations of these data for both elemental and isotopic Nd distributions. We discuss the implications such a benthic flux model carries for interpretation of Nd isotope data as a tracer for understanding modern and past changes in ocean circulation.

Keywords: rare earth elements, neodymium isotopes, marine geochemistry, benthic flux

INTRODUCTION

Neodymium (Nd) isotopes (denoted ε_{Nd}, which reflects the $^{143}Nd/^{144}Nd$ ratio normalized to a Chondritic Uniform Reservoir; Jacobsen and Wasserburg, 1980) are widely recognized as a valuable tracer for ocean circulation (e.g., Piepgras and Wasserburg, 1980, 1987; Elderfield, 1988; von Blanckenburg, 1999; Frank, 2002; Goldstein and Hemming, 2003; Piotrowski et al., 2004; van de Flierdt and Frank, 2010). The potential for Nd isotopes to serve as a circulation tracer lies with the observation that ε_{Nd} distributions appear to mirror the pattern of global deep-water thermohaline circulation. These observations support the assumption that ε_{Nd} is conservative or "quasi-conservative" in the oceans and will trace water masses in a manner similar to temperature and salinity (Frank, 2002; Goldstein and Hemming, 2003). Furthermore, elemental Nd is assumed to have negligible bioactivity, although recent work suggests that there are important caveats to this assumption (Shiller et al., 2017). However, because of the concerted efforts invested into measuring neodymium in the oceans as well as within sedimentary archives, inconsistencies between the observed distributions and the assumptions inherent in the use of the Nd as a tracer are becoming increasingly apparent. The best known of these inconsistencies is the "Nd paradox" (Jeandel et al., 1995, 1998; Tachikawa et al., 1999a; Lacan and Jeandel, 2001). Described in many ways, this paradox fundamentally describes the contradictory observations that while ε_{Nd} appears to behave conservatively, the water column profile of dissolved elemental Nd ([Nd]) appears to reflect the behavior of a reactive element, showing a nutrient-like distribution (see discussion in Goldstein and Hemming, 2003). In short,

ε_{Nd} distributions imply a residence time of $\leq 10^3$ years, while [Nd] distributions imply a residence time of $\geq 10^4$ years (Bertram and Elderfield, 1993; Jones et al., 1994). This discrepancy appears in paired geochemical mixing models (Goldstein and Hemming, 2003) and models that attempt to reproduce the global distribution of ε_{Nd} (Tachikawa et al., 2003; Jones et al., 2008; Arsouze et al., 2009; Rempfer et al., 2011). In addition to the "Nd paradox," inconsistencies have arisen regarding past records of authigenic ε_{Nd}, which sometimes prove to be difficult to explain when assuming water mass mixing of fixed end-members (Osborne et al., 2014; Stewart et al., 2016), or show exceptional disparities between adjacent sites (Stumpf et al., 2010; Roberts and Piotrowski, 2015; Howe et al., 2016; Hu et al., 2016).

The problem with ε_{Nd} as a circulation proxy is fundamentally that while ε_{Nd} appears to trace water masses effectively, it is not particularly potent at discerning geochemical processes that might impact its distribution. For example, it is difficult to use ε_{Nd} to determine *how* a water mass acquires its isotope signature. Although the pattern of global ε_{Nd} mirrors that of thermohaline circulation the cause of that apparent coincidence is not straightforward. For example, that the deep North Pacific is a Nd isotope end-member for mixing is difficult to justify given that no deep water forms within this basin. If isotopic end members can develop unassociated with preformed properties of the water mass, then there is clearly a need to explain and constrain the effects of these processes on ε_{Nd}, especially for interpretation of ε_{Nd} as ancient records of circulation.

Relatively recently, several possible mechanisms for non-conservative behavior of ε_{Nd} have been forwarded: boundary exchange, Submarine Groundwater Discharge (SGD) and a benthic Nd flux (Lacan and Jeandel, 2005b; Johannesson and Burdige, 2007; Abbott et al., 2015a). These three hypotheses are all similar in that bottom water can be altered along the sediment-water boundary. Although these hypotheses may have been articulated as distinctly different, the differences among these hypotheses may be simply semantic or reflect our incomplete understanding of the processes involved. Boundary exchange, as described by Lacan and Jeandel (2005b) is typically thought to reflect an isotope exchange of Nd with net zero concentration change that occurs between the sediments and bottom water predominantly at ocean margins (Jeandel, 2016). While this model is highly cited, the specific mechanism or processes are not well defined. In contrast, both the SGD and benthic flux models propose more distinct mechanisms but lack the robust global data sets needed for verification. All three of these hypotheses invoke a potential source of dissolved [Nd] to the oceans from sedimentary fluids; SGD waters are considered here to be originally fresh waters, while the benthic flux model considers seawater as the source fluid origin. These latter hypotheses will differ in the quantity and location of the Nd fluxes they predict and the ε_{Nd} that they carry. Clearly, the distinctions among all three models is nuanced, and again, probably simply reflects the need for further investigation or even simple definition. However, all three models challenge the underlying assumptions around the conservative nature of ε_{Nd} in the water column.

A more comprehensive understanding of the marine geochemical cycle of REEs in conjunction with ε_{Nd} is needed to build more accurate geochemical models and interpret down core records with respect to ocean circulation. The problems arising from the notion of ε_{Nd} as a paleoproxy perhaps reflect the superficial, and perhaps data limited synthesis between analyses of ε_{Nd} and the rare earth elements (REEs) throughout the ocean basins. Fortunately, the comprehensive nature of the GEOTRACES water column sampling will go far to improve our understanding of water column processes that affect the REEs and ε_{Nd}. Here, we discuss published ε_{Nd} and Nd data from the Atlantic Ocean, with the intent to clarify our understanding of these tracers where they appear to be most robust. While we do not present any new data, we attempt to illustrate that a holistic view of published REE and ε_{Nd} distributions in the oceans is consistent with predominant control from a benthic sedimentary source. Our conclusion is that processes occurring within the water column (e.g., reversible scavenging) are likely a secondary control on ε_{Nd} or [REE] in the oceans, save where particle fluxes are exceptionally high, and that benthic fluxes exert primary control over the distribution of these elements and their isotopes.

MODERN OCEAN REES AND Nd ISOTOPES

It was originally held that the REEs are input to the oceans predominantly via rivers, with potential additions via dust where such inputs are relatively high (Byrne and Sholkovitz, 1996; Greaves et al., 1999; Tachikawa et al., 1999b; Goswami et al., 2014; Dunlea et al., 2015; Stichel et al., 2015; also see Bayon et al., 2004 for the alternative view that dust is a sink term). More recently, the emphasis of REE input to the oceans has shifted to greater consideration of a benthic continental margin source for REEs, as we will discuss further later (Spivack and Wasserburg, 1988; Jeandel et al., 1998; Goldstein and Hemming, 2003; Tachikawa et al., 2003; Arsouze et al., 2009; Rickli et al., 2009, 2010, 2014; Carter et al., 2012; Grasse et al., 2012; Singh et al., 2012; Grenier et al., 2013; Wilson et al., 2013; Garcia-Solsona et al., 2014).

In the open ocean, REEs are thought to be transferred from shallow to deep ocean via reversible scavenging on particles sinking through the water column (Elderfield, 1988; Byrne and Kim, 1990; Sholkovitz et al., 1994; Byrne and Sholkovitz, 1996). However, the heavier atomic mass REEs (HREEs, such as Yb, Lu) tend to have vertical profiles that are more "Si-like," which is thought to reflect the tendency for greater complexation across the REE series (Cantrell and Byrne, 1987; Elderfield, 1988; Byrne and Sholkovitz, 1996). Finally, removal of REEs from the ocean is thought to be predominantly via metal-oxides, although the role of organic matter, phosphates, or even carbonates, is likely to be important (Byrne and Kim, 1990,?; Byrne and Sholkovitz, 1996; Schijf et al., 2015). This model is considered the standard of marine REEs. Nd isotopes should also behave in a manner that is consistent with this model, although as pointed out previously this does not appear to be the case (Goldstein and Hemming, 2003; Jones et al., 2008; Arsouze et al., 2009). Successful efforts to reconcile the inconsistent behavior between elemental Nd and its isotopes, i.e., the Nd paradox, will likely

begin with an examination of these first principles of marine REE cycling.

The shift from considering riverine point sources to broad marginal inputs improves model results (Tachikawa et al., 2003; Arsouze et al., 2009) and offers an explanation for some of the irregularities observed when comparing Nd and its isotopes such as the constancy of surface ocean water ε_{Nd} (−7.8 upstream vs. −7.9/−8.0 downstream; Osborne et al., 2014) around the mouth of the Mississippi river that carries a far less radiogenic signal (at $\varepsilon_{Nd} < −11$; Goldstein and Jacobsen, 1987, 1988; Bayon et al., 2015. Budgetary estimates from diffuse benthic REE fluxes, such as SGD or from sedimentary pore water (Sholkovitz et al., 1989; Greaves et al., 1999; Haley and Klinkhammer, 2003; Tachikawa et al., 2003; Johannesson and Burdige, 2007; Schacht et al., 2010; Johannesson et al., 2011, 2017; Abbott et al., 2015a; Fröllje et al., 2016), suggest that they may dominate the flux of REEs to the oceans. Importantly, such diffuse, or at least hard to quantify, sources are consistent with deep-water isopycnal mixing of ε_{Nd} signals off margins that cannot be explained through surface water sources (Grasse et al., 2012; Grenier et al., 2013). However, while a diffuse benthic source of Nd appears to better describe the dominant flux of REEs to the ocean, outstanding questions remain. Arguably the most important of these is: what drives this flux? Any mechanism must be reconciled with the remarkably consistent REE pattern of seawater in light of diverse sediment compositions and sedimentary/diagenetic environments. As such, it seems unlikely that simple, unidirectional particulate dissolution can be the mechanism, because the dissolved REE pattern and ε_{Nd} would to some extent reflect such an input, following arguments posed by Sholkovitz (1993) and reiterated by Bau et al. (2013).

Another supposition in the current understanding of marine REE cycling is that reversible scavenging controls the vertical distribution of these elements in the water column. In his deeply insightful paper, Elderfield (1988) suggested cause for concern over this conjecture: not for shallow REE adsorption, but in light of a mechanism for desorption at depth. For many trivalent cations the pH-edge/Langmuir-front for adsorption onto particle surfaces lies well under a pH of 7 (Morel and Hering, 1993; Ngwenya et al., 2010); thus, over a typical oceanic pH range of 7.6 and 8.2 desorption is unlikely. The thermodynamics of desorption become even less favorable as the increasing dissolved concentration at depth would tend to push the equilibrium toward further adsorption (reiterating arguments posed by Elderfield, 1988). Moreover, given free Nd is <16% of the total dissolved Nd (Millero, 1992; Schijf et al., 2015), and surface adsorption coefficients are typically not exceptionally high (in the range of 3 to 5 onto carboxyl and moncarboxylic groups; Smith and Martell, 1989; Byrne and Kim, 1990; Ngwenya et al., 2010), the potential for REE transfer from the shallow to deep ocean via particle surface scavenging should be limited (Elderfield and Greaves, 1982; Stichel et al., 2015).
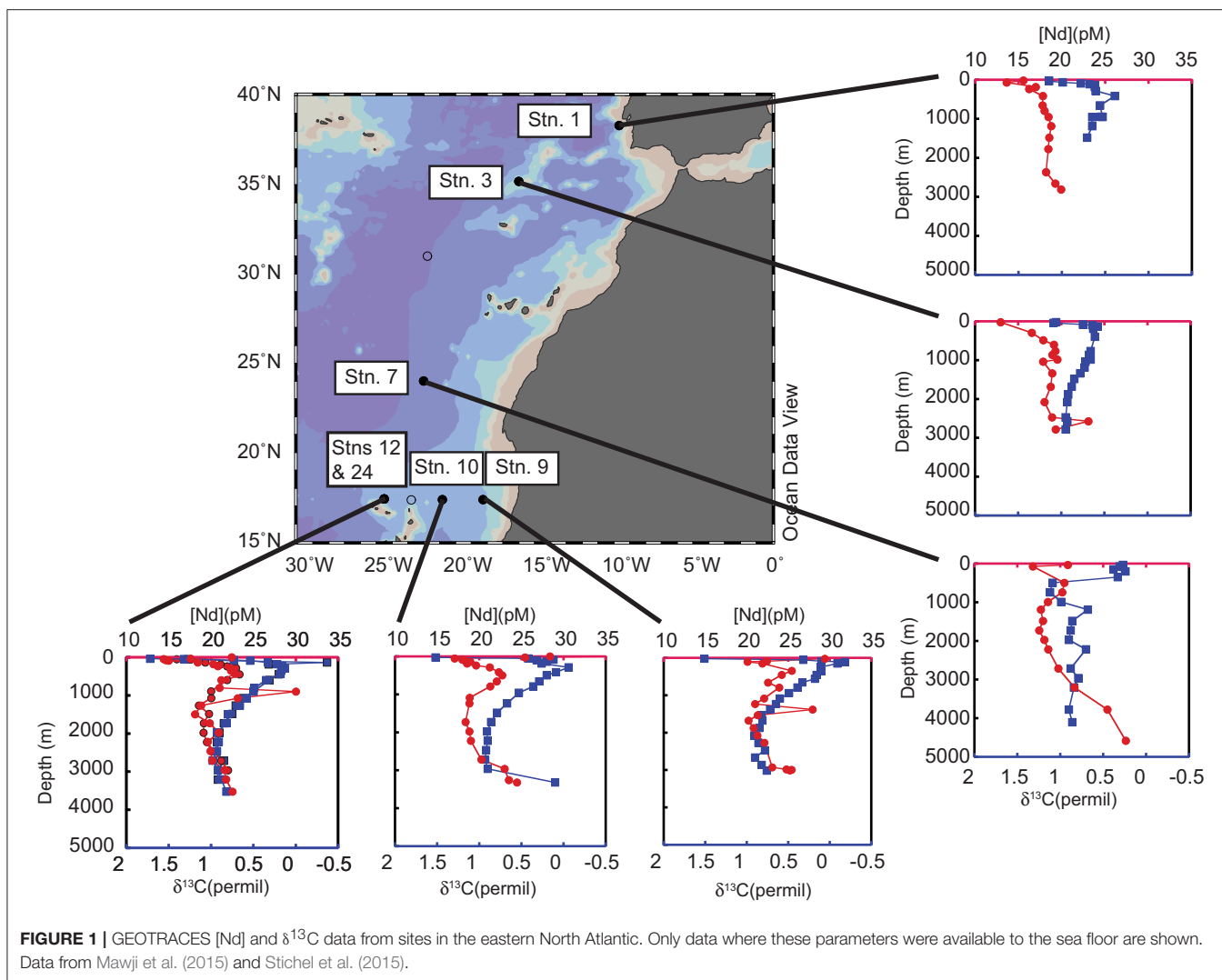
In spite of such arguments, lab and field observations attest that the REEs are indeed highly susceptible to adsorption (Sholkovitz, 1989), and that adsorption onto particles in the ocean certainly does happen (e.g., Sholkovitz et al., 1994; Tachikawa et al., 1999a). One positive test for REE adsorption

in the oceans may be seen in conservative Arctic Ocean REE profiles where particles are near absent (Yang and Haley, 2016). We do note, however, that a counter-argument can be made in that there does not appear to be an appreciable difference in the [Nd] profiles relating to marginal sites vs. distal sites, where particle loading may be very different (German and Elderfield, 1990; Grasse et al., 2012; Goswami et al., 2014; Haley et al., 2014; Abbott et al., 2015b; Stichel et al., 2015).

Considering all the arguments and data, a preferred model is that REEs are most likely transferred from the ocean surface to depth through incorporation onto complex organics, such as humic acids, polysaccharides, or other complex organic molecules that have binding coefficients higher than simple carboxyl groups (logK > 9; Byrne and Kim, 1990; Stanley and Byrne, 1990; Davranche et al., 2005; Pourret et al., 2007; Schijf et al., 2015). In this way, scavenging is actually achieved via an organic coating carrier phase that is remineralized, thus offering a mechanism for transfer of REEs from the particulate to dissolved phase without subsequent re-adsorption (i.e., not a desorptive process, but a remineralization; Sholkovitz et al., 1994). This model implies that [Nd] should behave much like $\delta^{13}C$ in the water column, wherein their distributions reflect a preformed signal modified by top-down uni-directional input additions related to POC remineralization. Available GEOTRACES data allow us to make an initial comparison of water column [Nd] and $\delta^{13}C$ (Mawji et al., 2015; Stichel et al., 2015; **Figure 1**). We consider the comparison inconclusive; these data appear to share many similarities (e.g., at Stations 12, 24, 10, especially in the upper 1,000 m) but not everywhere (e.g., at Stations 1, 3, and 7). Comparison of these [Nd] and $\delta^{13}C$ data yields no correlation ($r^2 < 0.05$; Figure S1), although the fit of all the data from the upper 50 to 500 m, ostensibly under highest remineralization, is better ($r^2 \sim 0.4$; Figure S2), which would support scavenging of Nd on isotopically light-C POM. The form of the [Nd] profiles in **Figure 1**, especially in the upper 1,000 m, does appear to share many of the characteristics of POM remineralization in the oceans (e.g., Suess, 1980; Martin et al., 1987) and of AOU (discussed by Stichel et al., 2015). Unfortunately, global compilations, such as presented by Tachikawa et al. (2017), produce poor correlations between $\delta^{13}C$ and [Nd] ($r^2 < 0.001$; not shown), and the similarity between deep (>1,000 m) [Nd] and P* (van de Flierdt et al., 2016) becomes difficult to justify under the hypothesis of POM scavenging of Nd.

A similar uni-directional release of REEs at depth can also potentially come from deterioration of the lithogenic minerals themselves (Rousseau et al., 2015; Abadie et al., 2017). This mechanism would differ markedly in its effect on water column [REE] and ε_{Nd} in comparison to a model based on an organic surface coating. Unfortunately, the evaluation of [Nd] and ε_{Nd} in light of a lithogenic source of Nd at depth has been ambiguous in the eastern North Atlantic (Stichel et al., 2015; van de Flierdt et al., 2016).

Evaluation of modes of scavenging may be complicated through multiple substrates for scavenging, each of which can deliver REEs to depth (e.g., complex organic molecules as well as lithogenic and biogenic silicates; Akagi et al., 2011; Akagi,

FIGURE 1 | GEOTRACES [Nd] and δ¹³C data from sites in the eastern North Atlantic. Only data where these parameters were available to the sea floor are shown. Data from Mawji et al. (2015) and Stichel et al. (2015).

2014). Adding additional ambiguity to the assessment of reverse scavenging is the issue of preformed REEs at depth that are likely conservative in nature (Haley et al., 2014; Zheng et al., 2016). Such preformed REEs must be an important component of deep water REEs (at least on basinal scales), such that REE profiles cannot be taken at face value: de-convolution of the conservative and non-conservative REEs is needed for accurate interpretation (Bertram and Elderfield, 1993; Haley et al., 2014; Zheng et al., 2016). Such efforts, either using a water mass approach (e.g., Bertram and Elderfield, 1993; Grasse et al., 2012; Stichel et al., 2012, 2015 or a more statistical approach (Singh et al., 2012; Haley et al., 2014; Zheng et al., 2016), are critical in evaluating the importance of scavenging on water column REEs. It goes beyond the scope of this paper to explore solutions for resolving preformed vs. "reactive" REEs. Our goal here is simply to suggest that much of the difficulty in resolving the "Nd paradox" is caused by undue emphasis placed on the function of reverse scavenging, which likely plays only a minor role in controlling the distribution of REEs and ε_{Nd} in the water column.

Our exemplar here is the outstanding work of Bertram and Elderfield (1993). These authors carefully evaluated the possible influence of scavenging and reverse scavenging, largely under an assumption of "top down" forcing, because of the similarities to Si and a lack of sedimentary data (Bertram and Elderfield, 1993). Their conclusion is that particle-water exchange is necessary to explain deep ocean ε_{Nd}, and give two possible mechanisms: a "top down" possibility wherein scavenged Nd exchanges over time in the deep ocean and a "...second option [that] simply places the site of exchange close to or within the sediment-porewater system with exchange within the nepheloid zone or transport via diffusion into overlying seawater" (Bertram and Elderfield, 1993). [Interestingly, the authors also note that "the simple (water density) & Si-REE correlations seen in bottom and near-bottom waters may also imply involvement of a benthic source. Unfortunately, no satisfactory data are available on REEs in oxic porewaters."].

Finally, regardless of the impact on the water column, we emphasize that all of the potential "top down" mechanisms for remobilizing surface REEs at depth would be greatly enhanced

within seafloor sediments (Freslon et al., 2014); i.e., manifest as a pore water flux. In summary, while scavenging certainly happens on particles, we argue that the REE mass transfer is likely relatively small and subsequent desorption at depth in the water column is unlikely. On the other hand, any such desorption or remineralization mechanism is likely to be significant in the sediments, where the chemical environment can change significantly.

BENTHIC CONTROL

Regardless of the discussions presented above, mechanisms driven via a "top-down" flux of REEs return to the disparity between ε_{Nd} and [Nd] as discussed by Goldstein and Hemming (2003). The question is fundamentally how can such processes occur that account for [Nd] distributions, yet does not obviate the conservative qualities of ε_{Nd}? That a water mass such as North Atlantic Deep Water (NADW) can maintain its signature on ocean-basin scales is arguably less justifiable in a "top-down" explanation of marine REEs than it is in the "bottom-up" explanation that will be discussed below.

If we consider our prior argument that reversible scavenging does not significantly impact Nd's water column distribution, what then can explain the distribution of [Nd]/ε_{Nd} at depth? A "bottom up" hypothesis argues that Nd and ε_{Nd} are truly conservative below the permanent thermocline, except when exposed to a benthic flux. This benthic flux will certainly impact overlying bottom water, but its influence may also be carried laterally along isopycnals, for example off the continental slope (as indicated by Grasse et al., 2012; Singh et al., 2012; Stichel et al., 2015). The interaction with the sediments is then what makes ε_{Nd} "quasi-conservative," vs. being truly conservative, as has been suggested previously (Lacan and Jeandel, 2004b; Abbott et al., 2015a). The two important aspects of this suggestion are that (1) in the absence of a positive benthic flux, Nd and ε_{Nd} will behave conservatively and (2) the ocean biogeochemistry of Nd and ε_{Nd} is thus defined by benthic diagenetic processes. That is, this benthic control model suggests that the REEs and ε_{Nd} are controlled by the nature of the benthic flux, which can be a positive, negative, or neutral term.

The idea of a benthic source for REEs, as described previously (Abbott et al., 2015a), would certainly help resolve model and observational inconsistencies of REE in the Pacific Ocean (Jones et al., 2008; Arsouze et al., 2009), but is such a source necessary anywhere else-in the Atlantic, Indian, Arctic or Southern Oceans? The North Atlantic, for example, has been well described in "top-down" models (Jones et al., 2008), or even through simple conservative mixing (van de Flierdt et al., 2016). Although we note here that the Denmark Straits is the 'birthplace' of the very non-conservative boundary exchange hypothesis (Lacan and Jeandel, 2004a,b, 2005a) and that other models have required benthic source fluxes in the North Atlantic (Tachikawa et al., 2003).

Why then invoke a benthic model? First, if correct, the benthic model would provide a mechanism to reconcile the apparent conflicts in our interpretation of Nd and ε_{Nd}; and second, the benthic model makes different predictions about how changes in ε_{Nd} and REEs records can be interpreted, when compared to a reversible scavenging model, as will be discussed later.

The concept of benthic control of [REE]/ε_{Nd} on Pacific waters is still a nascent idea (Abbott et al., 2015a, 2016; Du et al., 2016). Here, we expand on this idea in a general sense. First, benthic control of [REE]/ε_{Nd} will directly influence only the bottom water, such that a water mass detached from the bottom will maintain its ε_{Nd} so long as it maintains its temperature and salinity (i.e., *all* its conservative properties). Second, benthic control represents a diffuse boundary flux, which implies that deep water [REE]/ε_{Nd} distributions may be more disposed to being controlled by eddy diffusivity. Because eddy diffusion coefficients in the vertical are 10^{-5}-10^{-4} m^2/s (or greater; Ku and Luo, 1994), over hundreds to thousands of meters per year (horizontal coefficients are even greater), the impact of a benthic flux may potentially integrate over significant depths within the deep ocean. Furthermore, eddy diffusivity is also an order of magnitude higher on the seafloor relative to the water column because of the turbulence created by topography (Waterhouse et al., 2014); therefore, a benthic flux will be dissipated with great efficiency into the water column. This dissipation is the rationale for the observation that there is an apparent jump in REE concentrations between pore water and overlying water (Abbott et al., 2015b, 2016).

IMPLICATIONS OF A BENTHIC FLUX IN THE ATLANTIC

There is little direct observational data regarding the benthic REE flux to the oceans (Sholkovitz et al., 1989; Haley et al., 2004; Abbott et al., 2015b), and even less that tracks the ε_{Nd} of this flux. However, comparison with radium offers some support for the hypothesis. Again, the holistic nature of GEOTRACES sampling has provided rare, directly comparable Ra-REE-ε_{Nd} data (Charette et al., 2015; Stichel et al., 2015; USGT10/GA03 section from the Gulf of Cadiz to the Mauritanian coast). All isotopes of Ra positively correlate with [Nd] in the bottom water, although we plot only ^{228}Ra, as this isotope is most directly associated with a benthic source influence (**Figure 2A**). The correlation of ^{228}Ra with [Nd] in bottom water is strong ($r^2 = 0.7$ including all the data, and by omitting Site 7, $r^2 = 0.9$). Such a positive correlation is consistent with both ^{228}Ra and [Nd] sharing a common benthic source. In contrast, benthic ^{228}Th does not covary with [Nd], which might otherwise be expected if the source of deep Nd was delivered via top-down particle-based mechanisms.

Bottom water ε_{Nd} does not covary with Ra isotopes (**Figure 2B**). While such a correlation is not obligatory under the benthic control model, work with Pacific sediments suggests that certain components of the sediments may be more reactive during diagenesis, and such reactivity is also likely element specific (Abbott et al., 2016; Du et al., 2016). Thus, we might expect that reaction of these sedimentary elements imposes a co-variation between the magnitude and isotopic composition of the flux.
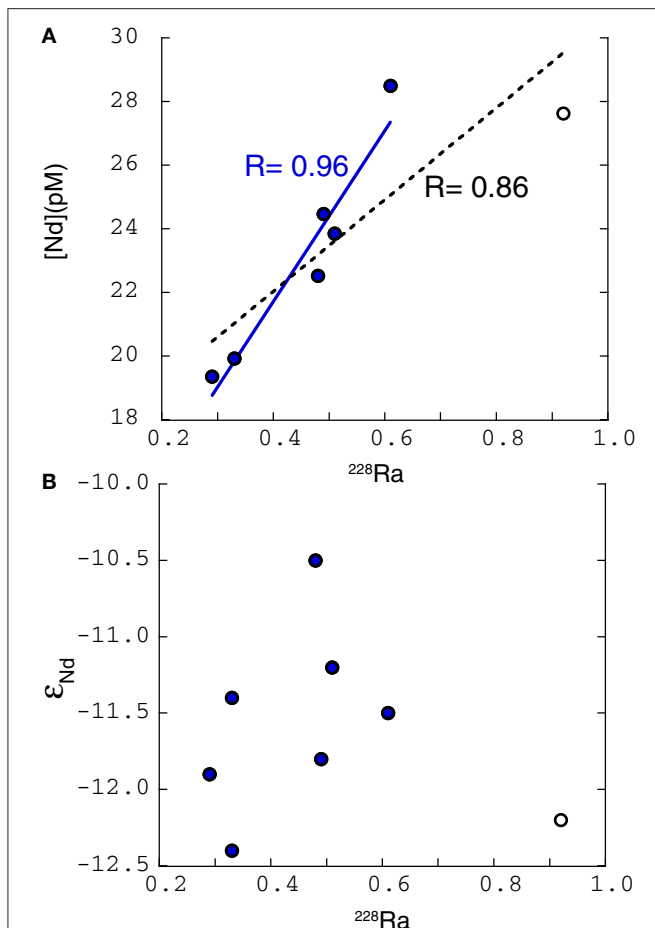
FIGURE 2 | Comparison of bottom water radium and neodymium (data from Charette et al., 2015; Stichel et al., 2015). **(A)** shows the positive correlation of the benthic-derived Ra with [Nd], consistent with a benthic source for both. **(B)** shows little correlation of ε_{Nd} with Ra, although a correlation may not be expected between these variables. The unfilled datum is arbitrarily isolated: there is no reason to consider this datum contaminated.

FIGURE 3 | Bottom water [Nd] and ε_{Nd} from Lambelet et al. (2016). Arrows show interpretation of flow paths of bottom water.

We reiterate that there is undeniable evidence in support of the idea that seawater ε_{Nd} traces basin scale modern water mass circulation, and the benthic control hypothesis suggested here does not detract or contradict these observations. On the contrary, we suggest that records of ε_{Nd} may potentially be used to actually quantify current velocities, given that the "exposure time" of a water mass to the bottom (Abbott et al., 2015a) implies a temporal sensitivity necessary to establish velocity. As an example, the bottom water data of Lambelet et al. (2016) for the North Atlantic, can be plotted vs. latitude (**Figure 3**). A benthic control based interpretation of these data may be that there are three diagenetic regimes in the North Atlantic: north of 55°N, between 45 and 55°N and south of 40°N. We will first focus on the increasing [Nd] and decreasing ε_{Nd} of the middle regime (~43°-55°N). In this region, there is a total change in ε_{Nd} of ~2 units, of which conservative mixing with LSW can account for ~1 unit (**Figure 4**; using water properties defined in van de Flierdt et al. (2016). Applying the simple exposure time model of
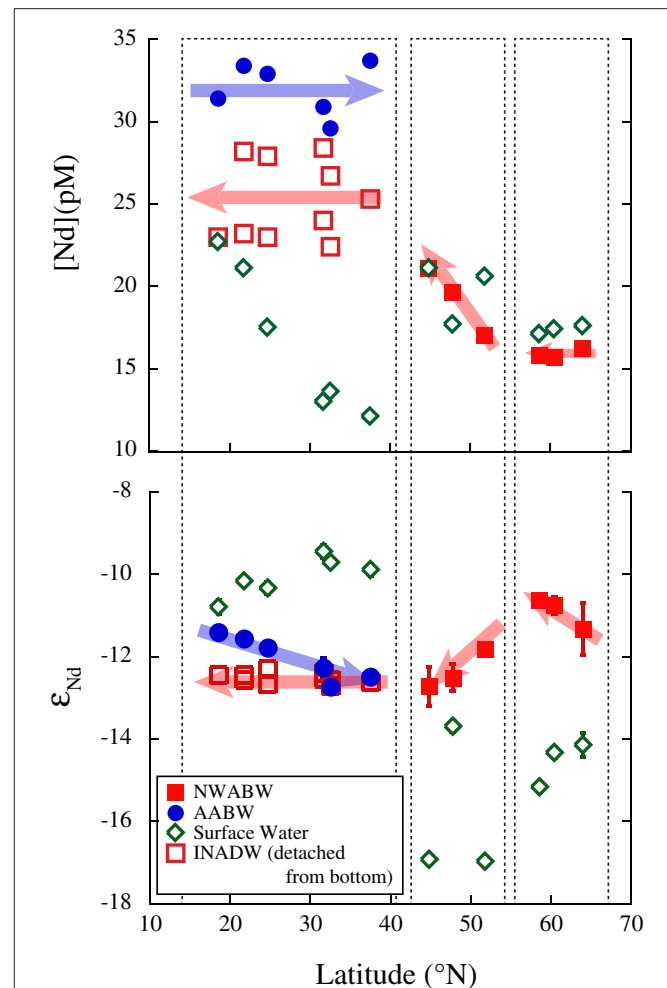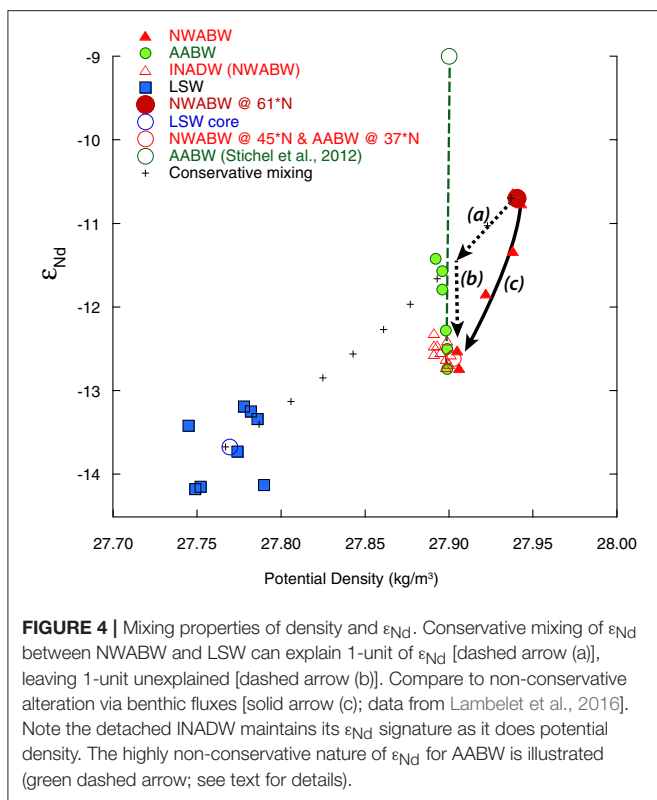
Abbott et al., 2015a; assuming flux of 20 pmol/cm^2/yr with ε_{Nd} of -15, which is reasonable but arbitrarily chosen, and a deep water [Nd] of 15 pM, which is measured), we might estimate that the residual 1-unit corresponds to ~35 years of benthic flux exposure on a 1 km thick bottom water layer, occurring over ~12° latitude. This combination results in a bottom water current velocity of 0.2 cm/s. This estimate of effective transport rate, despite its obvious simplifications and assumptions, is not incomparable to the 1.8–2 cm/s estimates derived from CFC and tritium/He^3 (Smethie et al., 2000; Steinfeldt and Rhein, 2004). This simple model scenario also predicts [Nd] of the water mass increases to 23 pM, similar to that observed (**Figure 3**). Other scenarios are obviously possible; for example, a 5 pmol/cm^2/yr flux with ε_{Nd} of -20 offers a similar 40 year exposure estimate, but predicts a final [Nd] of only 17 pM. The only existing pore waters from the Atlantic (Buzzard's Bay; Sholkovitz et al., 1989) show pore water [Nd] of >700 pM at ~13 cm depth in the sediment, which compares to fluxes as large as any seen in the Pacific (up to 30 pmol/cm^2/yr; Haley and Klinkhammer, 2003; Abbott et al., 2015b). Such a flux of

FIGURE 4 | Mixing properties of density and ε_Nd. Conservative mixing of ε_Nd between NWABW and LSW can explain 1-unit of ε_Nd [dashed arrow (a)], leaving 1-unit unexplained [dashed arrow (b)]. Compare to non-conservative alteration via benthic fluxes [solid arrow (c); data from Lambelet et al., 2016]. Note the detached INADW maintains its ε_Nd signature as it does potential density. The highly non-conservative nature of ε_Nd for AABW is illustrated (green dashed arrow; see text for details).

30 pmol/cm²/yr with an ε_Nd of −25, as implied might be the case in this region (Lambelet et al., 2016), predicts only 4 years of exposure for ~1 ε_Nd unit change, which equates to 1.1 cm/s velocity, but an increase of [Nd] to just 16 pM. Again, these calculations are obviously crude, and poorly constrained; we use them simply to illustrate sensitivity of deep water to benthic fluxes, and the feasibility of using the concept for quantitative reconstruction of circulation.

The Lambelet et al. (2016) data show constancy of ε_Nd in the Northwest Atlantic Bottom Water (NWABW) after it detaches (or is displaced) from contact with the bottom south of ~40°N. At these lower latitudes, Antarctic Bottom Water (AABW) is in contact with the sediments, and it is this southern-sourced water mass that appears to be modified during its transit northwards. While such a pattern can be explained with a benthic control model for [REE]/ε_Nd, a "top-down" process that clearly alters bottom water but not the deep water overlying bottom water seems difficult to reconcile. Moreover, the potential density of AABW is remarkably stable along its flow path: σ = 27.9 kg/m³ at ~60°S (Stichel et al., 2012) vs. σ = 27.903 kg/m³ at ~37°N (from Lambelet et al., 2016 data; **Figure 4**). This constancy indicates that little water mass mixing occurs during this bottom water transit, yet ε_Nd changes significantly: at least one unit in just the northern hemisphere data of Lambelet et al. (2016). Again, if we argue that conservation of NADW ε_Nd precludes a top down driver for AABW ε_Nd change, the logical conclusion is that benthic alteration impacts bottom water (i.e., AABW) ε_Nd. Through the same approximations done above (assuming an arbitrarily chosen 5 pmol/cm²/yr flux with ε_Nd of −15 and

measured 30 pM [Nd] of bottom water), we might estimate that the 1-unit Δε_Nd of AABW observed corresponds to ~150 years of exposure. Over 25° of latitude, this corresponds to a current velocity of 0.06 cm/s, implying that AABW has about one third the velocity as NWABW. (Note that because this calculation is based on a concentration gradient, the exact positions of where the slope is calculated can differ, making such estimations amenable to paleo-reconstructions where end-members may not be well constrained.) This effective transport rate estimate is, as was the case for our NADW estimate, lower than the CFC estimate of ~1.2 cm/s for AABW (Haine et al., 1998). We can predict that the benthic fluxes affecting AABW must be more complex, because linear extrapolation of the rate of change in ε_Nd over latitude as shown in **Figures 3, 4** would imply that AABW has an ε_Nd of −6 at 60°S, which it does not (Stichel et al., 2012). The likely rationale for this difference is that the diagenetic fluxes along the greater AABW flow path are more nuanced in both their magnitude and composition than can be expressed by our simplified approximations.

There are three further points relevant to this discussion. First, the benthic control hypothesis does not invoke water mass mixing to explain patterns in ε_Nd such as those shown in **Figures 3, 4**) That is, there is no obligate change in conservative properties, such as temperature or salinity, as the bottom water ε_Nd is modified. Again, mid-depth water masses detached from the sediment will likely maintain their ε_Nd signatures, or mix them as they would other conservative tracer properties along isopycnals, for example.

Second, the North Atlantic appears to have a propensity to mask the impacts of a benthic flux because ventilation rates are high, and thus exposure times are low. Instances where benthic influences may be directly observed in the North Atlantic (e.g., Lacan and Jeandel, 2004c) would thus reflect rather extreme cases of high flux or divergent isotopic composition. In contrast, AABW in the South Atlantic (and PDW in the Pacific) circulate rather more slowly and thus would be prone to longer benthic exposure, resulting in more obvious impacts of a benthic source flux.

Third, the benthic flux mechanism seems to be intimately connected to authigenic metal oxides in the sediments (Abbott et al., 2016), which appear to modulate the REE flux and its ε_Nd signature. Authigenic metal oxides appear to act as a "capacitor" of REE: i.e., both a source and sink of pore water and bottom water REE. Analogous to electrical capacitance, more abundant sedimentary metal oxides will produce greater Nd fluxes with less temporally variable ε_Nd signatures (Abbott et al., 2016). While this mechanism is clearly far from resolved, it offers an explanation for the apparent lack of influence from the non-radiogenic lithogenic sediments of the central North Pacific (Jones et al., 1994). Specifically, we predict that there is no positive benthic flux from these sediments, or that reactive diagenetic materials are not present in these sediments (Abbott et al., 2016; Du et al., 2016), or both. We also note that the non-radiogenic Nd data presented by Jones et al. (1994) reflect the post-leach lithogenic fraction of the sediments, which may not play a role at all in defining the benthic flux as defined by our proposed mechanism.

PALEOPROXY Nd

Arguably the most important implication of benthic control on marine [REE]/ε_{Nd} is how we interpret paleoceanographic records of water mass change. For these studies, the difference between a "top-down" or "bottom-up" control on bottom water and on the marine budget of REEs becomes paramount for two reasons:

Firstly, most interpretations of paleo-data treat ε_{Nd} as fundamentally conservative, discounting the possibility of changes in REE supply that is not the result of water mass mixing or circulation. In a reversible scavenging model, this may be a valid assumption if deep-water sensitivity to surface ocean change is small. However, this supposition then begs the question of why reversible scavenging controls the modern deep [REE]/ε_{Nd}? On the other hand, in a benthic control scenario the ε_{Nd} of bottom water may evolve through non-mixing processes: such as a change in the benthic flux or a change in the "exposure time" of the bottom water to this flux (Abbott et al., 2015b). As such, an ε_{Nd} record interpreted through a benthic control model may reflect a change in benthic flux or exposure time, the latter of which may well be the result of changing circulation patterns or velocities. Despite the ostensible complications, we argue that interpreting ε_{Nd} records purely as a conservative tracer discounts the "pseudo-conservative" nature of the tracer. Our benthic control model offers an internal cycling constraint on [Nd] and ε_{Nd} compared to a reverse scavenging model. Both models require the ability to reconstruct fluxes through time to accurately use ε_{Nd} as a tracer: the reversible scavenging model requires estimation of vertical particle fluxes and particulate type over time, whereas the benthic control model requires estimation of the benthic flux over time. Determining either of these fluxes will be non-trivial tasks, but may be resolvable.

Secondly, similarity between surface sediment archival phases (dispersed oxides, coatings, fish teeth, forams) and bottom water is often cited as evidence for record fidelity under the top down model for ε_{Nd}. In the benthic control model, such correspondence will result from bottom water that is either dominated by a strong positive benthic flux, wherein the preformed bottom water ε_{Nd} signature is overwhelmed by a pore water signature supported by the authigenic phases, or from a negative or net-zero pore water flux, such that pore water and authigenic phases passively record bottom water signatures. There is also a range of intermediate conditions where ε_{Nd} of the archival phase may differ from bottom water, and where we would predict there is a significant, but not overwhelming, positive benthic flux into bottom water (e.g., Du et al., 2016 in the Pacific, or Gutjahr et al., 2008; Huck et al., 2016 in the Atlantic). The relationship between authigenic phases (used as archival records) and contemporaneous bottom water is far more complex in the benthic control model, because the authigenic phases associated with diagenesis are intimately associated with the nature of the benthic flux that impact the bottom water signal (Abbott et al., 2016). Moreover, the concentrations of sedimentary reactive particulate phases, pore water, and bottom water differ by orders of magnitude, so we stress the importance of looking at both ε_{Nd} and the [REEs].
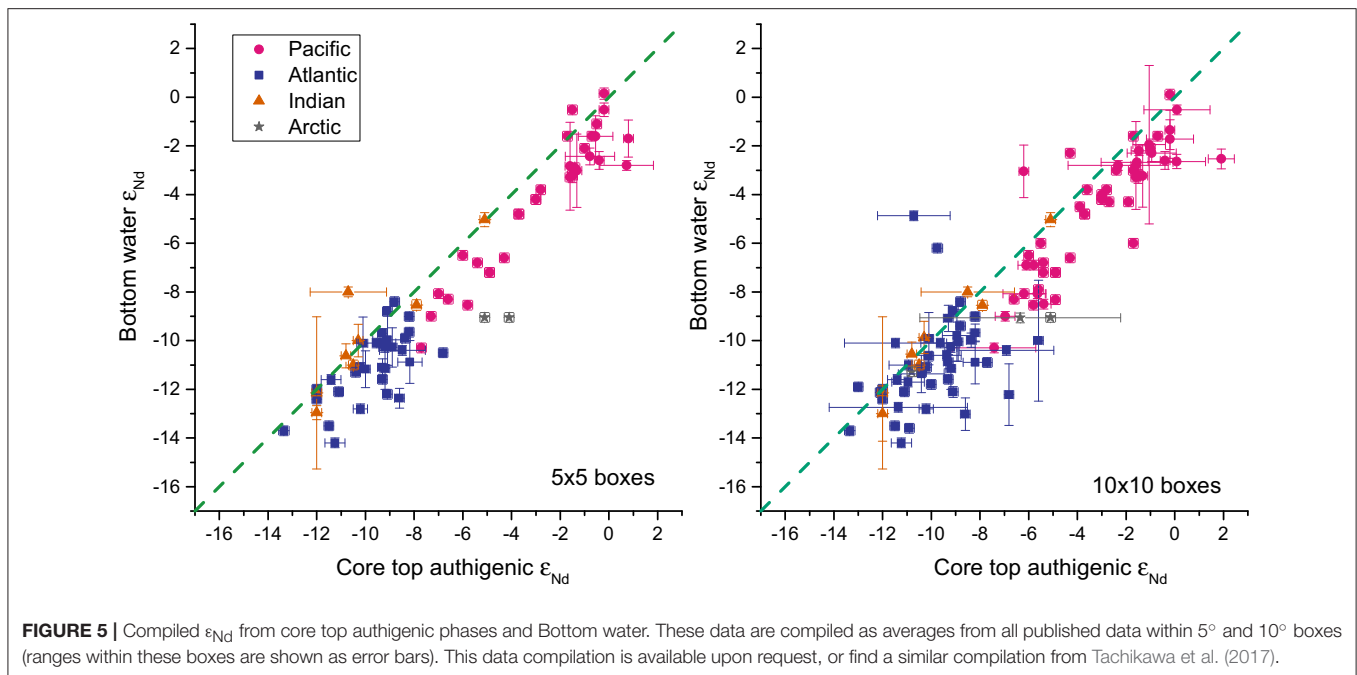
Our benthic model may give an initially grim outlook for paleoproxy work, but the situation is probably not at all intractable: in fact, these challenges are likely to be fully resolvable with further observations and models. Most pressing is the need to better determine the mechanisms and sources that define the Nd sink terms within the sediment column: these processes are ultimately what will define the proxy records. For example, Abbott et al. (2015b) did not discuss the deep (∼10 cm) sink term seen in pore water [Nd] profiles; if this sink records contemporaneous pore water ε_{Nd}, an apparent temporal offset could be generated in records of ε_{Nd} from diagenetic Fe-Mn oxides and other isotope and trace element proxies archived in the calcite lattice of foraminifera (Piotrowski et al., 2005).

Theory and observations all indicate that some aspect of bottom water ε_{Nd} is maintained in authigenic phases, and is likely identifiable in all sediment (Gutjahr et al., 2007; Wilson et al., 2013; Blaser et al., 2016; Du et al., 2016). Furthermore, the additional Nd generated through diagenesis should be far less variable and readily constrained as "baseline" variations in sedimentary records, vs. higher-order changes that are derived from seawater; analogous to Sr isotope records. A compilation of global surface sediment authigenic-phase ε_{Nd} vs. bottom water ε_{Nd} (**Figure 5**) illustrates that authigenic (archival) phases do trend with bottom water globally, but there is a remarkably uniform 1-ε_{Nd} unit offset toward authigenic phases being more radiogenic: an offset equivalent in the Atlantic and the Pacific. Furthermore, we note that the Pacific data actually have a more robust correlation compared to the Atlantic data, consistent with the preceding discussion that benthic fluxes in the Atlantic are more difficult to identify from bottom water data. Bearing in mind that the concentration of Nd in the authigenic phases (at ppm Nd) is nominally six orders of magnitude greater than the bottom water (at pM Nd), it is difficult to explain these data without invoking a Nd source from within the sediments that is globally persistent. Of course, there are many outstanding questions to answer before better understanding the benthic flux of REEs and ε_{Nd}: for example, can a flux be more non-radiogenic than the sediment host? How do these fluxes change over time?

In summary, while complex, diagenesis does follow predictable rules that make it amenable to modeling, which, in turn, can provide a robust estimation of past changes in the benthic control on bottom water Nd. In turn, these modeled boundary conditions can be used to calculate current direction and velocities as suggested in the modern examples above. Moreover, such studies may provide further evidence for changes in pore waters that can relate to changes in ocean redox or acid-base chemistry. The benthic model adds complexity, but also potential for the application of [REE]/ε_{Nd}.

BEYOND THE REES AND ε_{Nd}

The REEs and ε_{Nd} are often touted as being excellent tracers of processes that impact marine geochemical cycles in a much broader sense. As such, the hypothesis of benthic control on deep ocean REE cycling may support suggestions for the importance

FIGURE 5 | Compiled ε_{Nd} from core top authigenic phases and Bottom water. These data are compiled as averages from all published data within 5° and 10° boxes (ranges within these boxes are shown as error bars). This data compilation is available upon request, or find a similar compilation from Tachikawa et al. (2017).

of these diagenetic processes in marine geochemical cycles in general. For example, the same authigenic Fe/Mn oxides apparently involved in the marine cycling of [REE]/ε_{Nd} are also rich in other trace metals (e.g., Cu, Zn, Ni, Co). These authigenic metal oxides may be acting in an expansive way as a capacitor for geochemical fluxes; i.e., as both a source and sink of these trace metals.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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SUPPLEMENTARY MATERIAL

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